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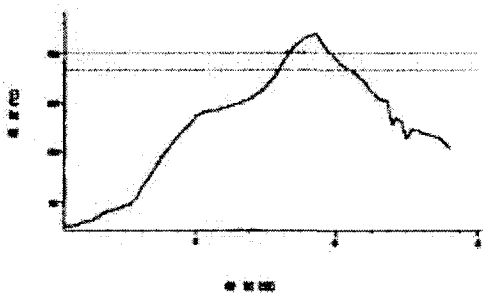
(54) MANUFACTURE OF PRINTED CIRCUIT BOARD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a film which is high in discoloration resistance and solderability by a method wherein a metal pad and/or a through-hole is protected in a PCB manufacturing method.

SOLUTION: It is preferable that a pad and/or a through-hole is gloss-etched through a dipping method, and the pad and/or the through-hole is plated with metal and treated with discoloration preventing agent. Discoloration preventing agent may be incorporated in a dip plating bath. A metal plating process is usually carried out with silver or bismuth, and the pad and/or the through-hole contains copper.



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CLAIMS

[Claim(s)]
[Claim 1]Coat PCB which contains an insulating layer and a conductive layer with a metaled pad and/or a run through hole, and here, Are the method of giving a coat of an antitarnish agent to this pad and/or a run through hole, and in a stage of gloss etching. In an immersion metal plating stage which forms a plated surface of metal which can be soldered contacting-to gloss etching constituent-this pad and/or run through hole;, and after that. A method including carrying out metal plating of a pad and/or a run through hole which were etched by making a plating constituent which does not contain a reducing agent to this ion substantially contact including ion of metal whose degree of electropositive is higher than metal which forms this pad and/or a run through hole.
[Claim 2]A method according to claim 1 of contacting the surface of plated metal in a solution of an antitarnish agent.
[Claim 3]Coat PCB which contains an insulating layer and a conductive layer with a metaled pad and/or a run through hole, and here, In a metal plating stage which forms a plated surface of metal which is the method of giving a coat of an antitarnish agent and can be soldered to this pad and/or a run through hole. A method including carrying out metal plating of a pad and/or a run through hole which were etched by making a plating constituent contact, and contacting a plated surface of metal in a solution of an antitarnish agent.
[Claim 4]A method according to claim 3 of being the way a metal plating stage contains ion of this metal with the higher degree of electropositive for this pad and/or metal whose degree of electropositive is higher than metal of a run through hole, and carries out immersion/substitution coating of the reducing agent to this ion from solution which is not included substantially.
[Claim 5]A complexing agent [as opposed to this ion in a plating constituent], a method according to any one of claims 1 to 4 of containing a polydentate ligand complexing agent

preferably.
[Claim 6]A way according to any one of claims 2 to 4 a plating constituent contacts a surface of metal in a solution containing an antitarnish agent so that an antitarnish agent may exist in a metal plating constituent in this method including an antitarnish agent in the case of a plating stage.
[Claim 7]A method according to any one of claims 2 to 4 of contacting a plated formed surface of metal in a solution which forms the surface by which metal plating was carried out in a plating stage, and contains an antitarnish agent in the second phase after washing after that.
[Claim 8]Claims 2-4 whose contact time of a solution containing an antitarnish agent and a plated surface of metal is 10 seconds - 5 minutes, a method given in any 1 clause of 6 or 7.
[Claim 9]Claims 2-4 which contact a surface of metal in a solution containing an antitarnish agent by dip coating or spray painting, and a method given in any 1 clause of 6-8.
[Claim 10]Claims 2-4 to which an antitarnish agent exists in this solution in 0.001 to 5weight % of quantity of a solution, and a method given in any 1 clause of 6-9.
[Claim 11]Coats of plated metal of a surface of metal are nickel, silver, tin, lead, palladium, cobalt, gold, platinum, bismuth or those alloys, and the method according to any one of claims 1 to 10 of containing silver preferably.
[Claim 12]A method according to any one of claims 1 to 11 by which a pad or a run through hole is formed with copper.
[Claim 13]A method according to any one of claims 1 to 12 including a preliminary stage given so that it may mean that a pad and/or a run through hole exposed with as a mask which is an insulator to a trace of a conductor exposed on the surface of PCB.
[Claim 14]A method according to any one of claims 1 to 13 including a succession stage of attaching a conductive part to a pad and/or a run through hole which carried out metal plating using solder which carries out direct contact to metal plating.
[Claim 15]It is an aquosity plating constituent suitable for forming immersion plating of metal whose degree of electropositive is comparatively high in a ground of metal whose degree of electropositive is comparatively low, A constituent which contains a complexing agent to ion and this ion of metal with the higher degree of electropositive, and an antitarnish agent to this metal with the higher degree of electropositive, and does not contain a reducing agent to this ion substantially.
[Claim 16]The constituent according to claim 15 in which an antitarnish agent exists in a solution in 0.001 to 5weight % of quantity of a constituent.
[Claim 17]These ion is nickel, silver, tin, lead, palladium, cobalt, gold, platinum, bismuth or those alloys, and the constituent according to claim 15 or 16 that is silver ion preferably.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]A "bare board" is produced in the first phase (multistage story), in the case of manufacture of a printed circuit board (PCB), it is the second phase (multistage story), and it attaches various parts to the board. This invention relates to the culmination in manufacture of a bare board which covers a bare board with a protective layer, before progressing to the second manufacturing stage.
[0002]
[Description of the Prior Art]In order to attach parts to a bare board on a second stage story, there are the twist latest surface installation devices, such as part [of the present dimorphism type]:, i.e., an owner leg article, for example, a resistor, and a transistor. An owner leg article attaches each of a leg to a board in the hole of a board through and by ranking second and securing that the hole around a leg is filled with solder. A surface installation device is attached on the surface of a board by soldering in a flat contact portion region, or adhesion using adhesives.
[0003]In the first phase, the board containing the pad and/or run through hole of an insulating layer, a conductive circuit diagram form, and conductivity is manufactured. A board may be a multilayer board which has arranged two or more conductive-circuits figures between insulating layers, or may also include the insulating layer of one layer, and one conductive-circuits figure.
[0004]A run through hole may carry out through plating so that they may be conductivity, and the pad which forms surface installation parts or the region attached in a subsequent part attachment stage may also be conductivity.
[0005]Although a circuit diagram form, a pad, and the conductive region of a run through hole may be formed with the mixture of what kind of conductive material or a different conductive

material, they are generally formed with copper. Temporally, copper oxidizes, and soldering fitness is held, before advancing to the second part attachment phase, since there is a tendency which forms the layer of the copper oxide which has inferior soldering fitness, Preventing formation of the surface layer of the copper oxide whose soldering is easily impossible covers a desirable pad and/or region of a run through hole, and a protective layer is coated.

[0006]In order to produce a bare board, there are two or more methods, but one of the methods most widely used for production of a bare board is publicly known as the technique of "being a wrap solder mask about bare copper" (SMOBC). Generally such a board contains the epoxy joint fiberglass which covered one side or both sides with the conductive material. It seems with it being general that this board is a multilayer board which has by turns a conductive layer containing a circuit diagram form and an insulating layer. a conductive material -- general -- a metallic foil -- it is copper foil most ordinarily. In the SMOBC technique, such a board comes to hand and a plate is punched using a template or an automation drill press. Subsequently, "through plating" of the hole is carried out using the non-electrolytic copper plating method which deposits a copper layer to whole board:, i.e., the both sides of the upper surface of foil, and the surface of a run through hole.

[0007]Subsequently, the region which covers a plate with a photosensitive thin film (photoresist), is made to expose by the preselected region, was developed chemically and was not made to expose is removed, and the conductive region which is the run through hole and pad which were plated is exposed. The thickness of the metallic foil of a region which is the following stage and was generally exposed by the electroplating stage of another copper is made to increase. The protective layer of the etching resist which is usually an electroplating composition of a ****- lead alloy is exposed, and the region of the thickened copper is covered and given.

[0008]Subsequently, copper for removing and removing photoresist is exposed, the surface of the exposed copper is etched and removed using a copper etching composition, and it leaves copper to the circuit diagram form needed for the last target.

[0009]The resist of a ****- lead alloy is stripped off in the following stage.

[0010]Since parts will be attached to a copper circuit trace, although parts are attached to not a trace but a run through hole, and a pad, generally, to coat solder is only needed. Therefore, by the development which follows screen printing or optical image formation, for example, and a case, using the technique of hardening, a solder mask is given to a board and the region which does not need solder coating is protected. Subsequently, the copper which the hole and the pad exposed is purified and it prepares for solder coating.

Then, for example, by hot wind smoothing (HAL) following the immersion to a solder bath, a protection solder coat is coated and a protection solder coat is formed in the region which is

not covered with a copper solder mask.
In order that solder may not wet a solder mask, a coat is not formed in the upper bed of the region protected by the solder mask at all.
[0011]In this stage, a board contains the insulating layer of at least one layer, and the conductive layer of at least one layer. The singular number or two or more conductive layers include a circuit trace. A board also contains the singular number or two or more pads and/, or the run through hole protected from discoloration by the layer of solder. A single conductive layer may include a circuit trace, either of the pads, or both sides. Do any pads become a part of conductive layer which is an outer layer of a multilayer board? The circuit trace on a board is covered with a solder mask.
[0012]Such a board can be promptly advanced to the second stage story for attachment of parts. In this second stage story, generally, by printing, the soldering paste (solder and a fusing agent are included) of one layer is applied to a board, and :, i.e., the start, which attains attachment of parts using solder arranges parts to the printed board. Subsequently, a board is heated within oven, fusion of the solder in soldering paste is occurred, and it forms the point of contact of parts and a board. This method is publicly known as reflow soldering. It replaces with this and the wave soldering method for passing a board over a melting solder bath is also used. In any case, it puts on any protection solder coats, and it uses additional solder.
[0013]The special necessity of attaching additional complication of the both sides of an owner leg article and a surface mounting device and the small parts in which many crowded has caused the demand to the surface-protection coat for the conductive metal which is going to attach the parts on PCB which grew. As for finishing which a bare board maker gives, it is indispensable not to leave the pad which has the surface which is not flat from it increasing the danger of electric failure. It is also indispensable that a protective film interferes in a subsequent solder stage, and there is nothing of a bare board and parts for which formation of a good conductive combination is barred by it. Probably, the excessive stage of removing a protective film will not be desirable.
[0014]The conductive metal surface must be formed with copper, must give the protection surface at the terminal point of the first step, and, generally, must prevent formation of the copper oxide in the copper surface before part attachment which cannot be soldered as explained above. Although especially this is important, it is because it is considered that the first step and the second part attachment phase are carried out at a thoroughly different generally part. therefore, ********** in few may exist between a conductive pad, and/or formation of a run through hole and a part attachment stage, and oxidation may occur in the meantime. Therefore, the protective film considered to make it possible to form the soldered point of contact when the soldering fitness of a conductive material is maintained and parts are attached to a bare board is needed.

[0015]"HAL" (hot wind smoothing) in which the most general protective film used now explained the example in full detail above -- they are the tin / lead solder generally given using law.

[0016]The HAL method is difficult to give solder uniformly, and since the thickness distribution formed by use of the HAL method makes it difficult to attach so that the very small parts which are used now and which crowded can be trusted, it is limited.

[0017]Some substitution processings to coating of the solder layer by HAL are introduced. The coat must enable formation of a reliable electric contact with parts. It must be equal to soldering of a multistage story. For example, as above-mentioned, although attached to a bare board, both an owner leg article and surface mounting parts exist now, and it seems with it being general that it is attached by at least two soldering operations. Therefore, a protective film must be borne also at at least two soldering operations so that the region which it is going to solder by the second operation may be protected in the case of the first operation and may remain.

[0018]As an alternative plan proposed to the solder of the tin/lead alloy used for the HAL method, there are organic protection and immersion tin or tin / lead plating, and nickel/gilding. In the method of nickel/gold, the primer layer of nickel is coated in copper.
Then, nonelectrolytic plating of a copper surface which coats a golden layer is carried out.
As for this method, many process steps exist and, moreover, golden use is inconvenient from causing an expensive process.

[0019]Organic protection to the copper pad in the storage before soldering and the case of an assembly is also carried out using the lacquer of a fusing agent. Generally the use is limited to the board (namely, board which has a conductive pad only in one field) of one side. Generally a coat is given by immersion, spraying, or roller painting. Since it is difficult to also give a steady coat to a misfortune on the surface of a board, it originates in the porosity of a coat, and the thickness of the coat which is not steady, and the limited life expectancy is caused. It has become clear that it has ****** in which fusing agent lacquer is also comparatively short.
Another problem will be a part attachment stage, and if it tends to use reflow soldering for attaching parts, it will be fixing parts to the proper place of the board bottom with adhesives. When fusing agent lacquer is thick, adhesives form combination between adhesives and the coat of lacquer instead rather than couple parts directly with the printed board. The strength of this combination may fall in the case of the stage of melting treatment and soldering, and may omit parts in the case of contact with a solder bath.

[0020]Another alternative plan in which it is used now is the passivation/protection processing based on use of the imidazole or triazole which forms a copper complex compound in a copper surface. Therefore, it combines with the surface chemically and these coats prevent the reaction of copper and oxygen. However, since this method has an unsuitable tendency in

bearing the stage of continuous soldering, it is inconvenient from there being a tendency that the subsequent soldering operation which needs the elevated temperature which reaches in the first soldering stage to destroy this layer and attach the parts beyond it cannot be borne. It is shown to the 0,428,383rd item gazette of the Europe public presentation patent by example of such a method, and here, It is the method of the surface treatment of copper or a copper alloy, and the way the number of carbon atoms includes that the surface of copper or a copper alloy is immersed in the benzimidazole compound which has an alkyl group of at least 3 in the position of 2, and the solution containing organic acid is indicated.

[0021]

[Problem to be solved by the invention]The method of giving a coat using the constituent containing silver is also publicly known.

[0022]Three kinds of general complexing systems for the unelectrolyzed silver plating method are systems based on either ammonia, thiosulfate salt or cyanide.

[0023]The solution of the ammonia system of the silver containing ammonia is unstable, and since there may be a tendency for an explosive azide to be formed, it is inconvenient. In order that the sulfur compound in the silver film formed may cause inferior soldering fitness, a thiosulfate salt system is a subsequent part attachment stage, and since an inferior electric contact may be formed between a bare board and parts, it is inconvenient to use in electronics industry.

[0024]Since plating liquid is poisonous, the system based on cyanide is inconvenient.

[0025]A U.S. Pat. No. 5,318,621 Description has disclosed the electroless plating liquid which contains amino acid as an accelerating agent as for which copper on a circuit board deposits silver or gold in a wrap nickel film. What neither will be directly plated for in copper is indicated from copper dissolving quickly the nonelectrolytic plating bath of gold or silver based on thiosulfate salt/sulfate, without making the coat of silver or gold form. "Metal Finishing Guidebook & Directory" (1993 editions) is considered by the introduction of these Cited documents. The silver plating liquid containing silver nitrate, ammonia, and a reducing agent like formaldehyde is mentioned.

[0026]The U.S. Pat. No. 4,863,766 Description is also indicating unelectrolyzed silver plating which uses the plating liquid based on cyanide. Russev has indicated immersion silver plating of the copper powder from the plating liquid containing silver nitrate and a nitrogen complexing agent by Metal Finishing and 27-30 pages per volume [81st] No. [the] (1983). In 53 pages of the Metal Finishing August items (1960), Geld ranks bright dip second to the ground of brass or copper first, and has indicated the painting method of the silver accompanied by the silver plating stage which plates a thick silver coat from the solution of silver nitrate and potassium iodide. This method is for plating an electric contact and raising conductivity.

[0027]In JP,H4-110474,A, base metal was plated with silver, and it dried, it ranked second,

processed with the mercaptan compound, and discoloration is prevented. In the 4,331,679th item Description of the Germany Request for a Patent. It coats by palladium by two steps of methods of making the bath which contains palladium salt, a complexing agent and formic acid, or a formic acid derivative on a second stage story including the first step to which the surface is contacted in the bath which contains palladium salt and an oxidizer for a base metal like copper contact. The latter bath may contain stabilizer for bath itself which stabilizes a bath to decomposition or a "plating piece." It is suggested that the ground which is copper must be beforehand etched using the non-gloss etching bath containing persulfate. However, the stage of such pretreatment tends to form the coat which is comparatively rich in porosity. This invention persons minimize the porosity rate of a coat using two steps of methods that a very thin coat is formed, in the first stage. This reference serves as warning to using silver for corrosion prevention for reasons of shift.

[0028]

[Means for solving problem]Metal with the higher degree of electropositive is the surface which it is going to coat, and this invention relates to substitution immersion metal plating which replaces metal with the lower degree of electropositive. The ion of metal with the higher degree of electropositive oxidizes the metal of a ground. By the single displacement by the metal in which the surface which it is going to protect can oxidize, and each relative electrode potential of a silver ion, since the substitution plating method forms a silver film on the surface of metal, it differs from a non-electrolytic decomposition process.

[0029]For example, although silver is plated with "present-day electroplating (Modern Electroplating)" (1963) by F.A. Lowenheim published by J. Wiley & Sons to almost all base metals by substitution, It is reported that the silver by which immersion plating was carried out is not a small adhesive property. F.A. Lowenheim has suggested that it is required to secure good adhesion of the layer of the silver in which the silver thin film was deposited for the raw material at the beginning, and electroplating of after that was carried out from the high cyanide shock bath, when a base metal is electroplated with silver.

[0030]An object of this invention is to provide the alternative plan over the protective coating by solder over the conductive surface of a bare board with required protecting from discoloration between the manufacturing stage of a bare board, and a part attachment stage.

[0031]

[Mode for carrying out the invention]According to this invention, coat PCB which contains an insulating layer and a conductive layer with a metaled pad and/or run through hole, and here, Are the method of giving the coat of an antitarnish agent to this pad and/or a run through hole, and in the stage of gloss etching. A method including carrying out immersion plating of the pad and/or run through hole which were etched in the metal plating stage which forms the plated surface of metal which can be soldered contacting-to gloss etching constituent-this pad and/or

run through hole; and after that is provided.

[0032]It seems that the insulating layer and conductive layer of PCB are as above-mentioned. They may also include the insulating layer of PCB of what kind of common use, and the figure of conductive circuits, respectively. The pad and/or run through hole for plating are a soldering stage for part attachment of after that of PCB, and in order to attach parts, they are a region which must maintain soldering fitness.

[0033]A gloss etching stage includes contacting a pad and/or a run through hole to a gloss etching constituent. Such a constituent forms the purified smooth surface that it is [the conductive metal in which it is known and a pad and/or a run through hole are formed for other uses] glossy in this industry. By contrast, a non-gloss etching constituent, for example, the constituent based on persulfate, gives the purified surface by which detailed surface roughening was carried out. Especially use of a gloss etching stage enables dense formation of the metallic film which is not porosity suitable for a subsequent soldering stage.

[0034]Generally a suitable gloss etching constituent is aquosity, for example, may be based on many mixtures from one kind or it among hydrogen peroxide, sulfuric acid, nitric acid, phosphoric acid, or chloride. A gloss etching constituent contains at least one kind of ingredient considered [tending to change the dissolution of copper to the inside of a gloss etching constituent, and] to be general.

[0035]Especially the suitable gloss etching constituent in which the surface of metal of a pad and/or a run through hole contains copper or a copper alloy, for example, the JP,62-188785,A-A No. 2 gazette (the inside of solution -- 5.1-10.2 mol/l. nitric acid.) 4.6-9.2 mol/l. sulfuric acid, 0.01 mol/l. of zinc nitrate, and a 0.4 mol/l. cupric nitrate -- content; JP,60-190582,A (for example, 20 to 50weight % of sulfuric acid (96%).) 10 to 25weight % of nitric acid (67.5%), 0.5 to 1weight % of chloride (35%), and 0.5 to 1weight % of a nonionic surface active agent -- a content; U.S. Pat. No. 3,668,131 Description (hydrogen peroxide.) sulfuric acid and a urea additive -- content;, [Metal Finishing and] 67-70 pages (potassium sodium.) of the 2 volume [84th] No. (February, 1986) Sulfuric acid, chloride, and diethyldithiosodium carbonate Content;Trans. Inst. Metal Finishing, 46-49 pages of the 2 volume [61st] No. (the summer of 1983) (acidification hydrogen peroxide containing hydrogen peroxide, sulfuric acid, and stabilizer); Oberflaeche Surf, the 20th volume -- the 8th -- No. (August, 1979) 178 -179 page (nitric acid and dodecylpyridinium chloride is contained); -- a U.S. Pat. No. 4,510,018 Description (sulfuric acid.) Hydrogen peroxide, Fatty acid amine and an ammonium compound. content; -- U.S. Pat. No. 4,459,216 Description (5-100g/l. of hydrogen peroxide, 100-300g/l. of sulfuric acid, and aromatic stabilizer are contained); -- JP,59-038308,A (0.15-0.3 mol/l. of chloride.) It is as given [0.2-0.4 mol/l. of phosphoric acid, and 0.02-0.1 mol/l. of sulfuric acid] in content. When the conductive material of a pad and/or a run through hole contains stainless steel, especially a suitable gloss etching constituent, Tr. Gos. Nauchno-Issled. Proektn. for

example, International-Publication patent No. 08317 [93 to] gazette; -- Provisional-Publication-No. (62)-238379-A No. 2 gazette; -- 1,928,307th item gazette [of the Germany public presentation patent]; -- or. It may be as Inst. Osnovn. Khim. and a description with a [93-97 pages] of of volume [36th] (1974). It is suitable when a conductive material is aluminum. ****** is as Met. Finishing and a 55-59 pages [of the 7 volume / 84th / No. (July, 1986)] description.

[0036]Therefore, what kind of glossy etching constituent which gives the purified surface may be used. In a gloss etching stage, the contact with a gloss etching constituent, For example, it is good by immersion at sufficient time to make it possible to form in the conductive material of a pad and/or a run through hole the surface with gloss which was indicated to either of above-mentioned reference document, and the temperature for which it was suitable, spraying, or any of other coating techniques. Generally, probably the temperature for contact with a gloss etching constituent is ordinary temperature, and probably there are 5 seconds - 10 minutes of contact time 30 seconds or more or 2 minutes or more preferably, and will be below for 5 minutes preferably.

[0037]Generally, the washing latter-part story subsequently directly advanced to a plating stage will exist, without generally drying including after an etching stage washing a bare board by deionized water. It may replace with this and may be made to contain, after rinsing a pickling stage.

[0038]A plating stage is an immersion (or substitution) plating stage.

[0039]In an immersion-plating stage, a plating constituent contains the metal ion of the metal whose degree of electropositive is higher than a conductive material. Therefore, it depends for selection of the metal ion in immersion-plating liquid on the metal which is going to be plated. Since a pad and/or a run through hole contain copper or nickel, as a suitable example of the metal to plate, they have bismuth, tin, palladium, silver, and gold, and, generally,; silver and especially bismuth ion are preferred for them.

[0040]Especially the suitable immersion silver plating method is indicated to the British patent application of the copending application of this invention persons for whom it applied to the 64th/of reference number basis of No. 2031/00 today.

[0041]As a metal ion source to plate, what kind of water-soluble metal salt, for example, a nitrate, acetate, sulfate, a lactate, or formate may be used. Preferably, silver nitrate is used.

[0042]Generally 0.06-32g (based on metal ion)/l. of ion [0.1-25g/l. of] which carries out metal plating exists in a plating constituent by the concentration of 0.5-15g/l. most preferably. 10-90 ** of 15-75 ** of contact of a surface of metal with plating liquid is preferably considered to come out at the temperature of 20-60 ** more preferably with it being general. For example, it seems that 15-50 ** of temperature of contact with plating liquid is 20-40 ** most ordinarily.

[0043]contact -- what kind of method -- it can also usually be based on immersion, spraying, or

level dip coating. Spray painting is preferred. Such contact may be a part of painting process which continues substantially.

[0044]The contact time of plating liquid with a surface of metal is enough to cover metal and form the plated surface of metal. It seems with it being general that contact time is 10 seconds - 10 minutes. It is found out that the contact time for less than 10 seconds generally gives the insufficient coverage by a silver film, and although contact time may be longer than 10 minutes, from contact time longer than 10 minutes, the further profits are not found out at all.

[0045]The suitable plating method is an immersion substitution method, and is not a true nonelectrolytic plating method. In the suitable plating constituent of this invention, the plated metal of one layer deposits on a pad and/or a run through hole with the metal plating ion in a solution as a result of the oxidation of the metal atom of the metaled surface. the time of this method covering all the parts of the surface of the metal which can oxidize with the metal which the plated metal plates -- the reaction beyond it, therefore since the deposit beyond it does not arise at all again -- self -- it is restrictive.

[0046]In the second mode of this invention, coat PCB which contains an insulating layer and a conductive layer with a metaled pad and/or run through hole, and here, In the metal plating stage which forms the plated surface of metal which is the method of giving the coat of an antitarnish agent and can be soldered to this pad and/or a run through hole. By making a plating constituent contact, a method including carrying out metal plating of the pad and/or run through hole which were etched, and contacting the plated surface of metal in the solution of an antitarnish agent is provided.

[0047]In this mode of this invention, preferably, before contacting a surface of metal to a plating constituent in a plating stage, a surface of metal is purified. Purification may be using what kind of publicly known purification constituent, acid purification constituent, for example, this technology. An example is PC1144 which is a regulator of the copper which Alpha Metals Limited supplies. When the purification stage using acid purification liquid exists, before contacting a surface of metal in plating liquid, generally a cleaning step will exist. Preferably, the stage before any purification will include a gloss etching stage.

[0048]In the mode of the both sides of this invention, since an antitarnish agent may exist in plating liquid itself, plating liquid contains the solution containing an antitarnish agent. Therefore, in the suitable method of this invention, the surface of metal plated on the occasion of a plating stage is contacted in the solution containing an antitarnish agent (namely, it may be contact in the case of formation of the plated surface of metal).

[0049]Or the surface of metal which formed the surface of metal and was formed after that in the plating stage again is contacted in the solution containing an antitarnish agent in another stage. A solution is aquosity preferably, and in deionized water, if there is nothing as if, it will be manufactured from pure water. The constituent containing an antitarnish agent may contain

additionally stabilizer, for example, a non-aqueous solvent, a surface-active agent, and/or a buffer for pH.

[0050]The contact with the constituent containing an antitarnish agent and the plated surface of metal will be for at least 20 seconds preferably for at least 5 seconds. When an antitarnish agent exists in plating liquid, generally the time of contact is determined by the temporal duration of a plating stage. Generally, probably, contact time is 1 to 5 minutes. 10-90 ** of temperature [15-75 ** of] of contact is 20-60 ** more preferably most ordinarily. For example, 15-50 ** of temperature of contact with plating liquid may be 20-40 ** most ordinarily. Contact is good also by what kind of idiomatic means, for example, immersion, spraying, or level dip coating.

[0051]the specific antitarnish agent in which until is used to some extent for most suitable pH -- however, it is dependent on the metal ion which exists mainly during the plating bath containing an antitarnish agent. When contacting an antitarnish agent to the plated surface of metal in a separate stage, to an antitarnish agent, pH is suitable, and it must be chosen so that it may not invade plating. When a solution is a silver plating constituent, convenient pH is within the limits of 3-10. When a solution is a bismuth plating bath, pH may be 1 or less than it.

[0052]The solution containing an antitarnish agent may be the last penetrant remover applied to a board before desiccation of a board. A board may be given to a subsequent processing stage after contact with the constituent containing an antitarnish agent. However, generally, a processing stage exists in the terminal point of the first bare board manufacturing stage, and after the contact with the solution containing an antitarnish agent and desiccation can carry out the second part attachment phase promptly. By a case, the cleaning step by deionized water may exist before desiccation, for example.

[0053]Probably, generally the concentration of the antitarnish agent in the solution containing an antitarnish agent is 0.0001 to 5 weight %/l., i.e., 0.001-50g. It seems with it being desirable that there is 0.005 to 3 weight % of quantity of an antitarnish agent most preferably 0.01 to 2 weight %, or less than 1weight %.

[0054]The method of the second mode of this invention may be used [as opposed to / wonderfully / gold, platinum, or the precious metals like a ruthenium], and will raise soldering fitness in that case.

[0055]In the second mode of this invention, a metal plating stage is immersion/substitution plating or a nonelectrolytic plating stage preferably. It consists of a single stage using a single plating constituent. Probably, a plating stage is immersion/substitution plating stage including contacting the metal of a pad and/or a run through hole to an immersion-plating constituent most preferably.

[0056]when plating is caused in addition to suitable immersion/substitution method, it is based, for example on nonelectrolytic plating -- if it becomes -- plating with an alternative plating

constituent -- public funds -- group ion, for example, nickel, may also be included.
[0057]Even when use of the antitarnish agent in this invention was stored at 96 hours or 150 ** with 40 ** and 93% of relative humidity for 2 hours, it became clear that the metallic film which has good color fastness (humidity and tolerance over oxidation) was given. As a result of porosity peculiar to dip coating falling by giving the smooth surface using a gloss etching stage, even in the elevated temperature which reaches in the case of a reflow-soldering process, the discoloration-proof characteristic is improved considerably. Although it originates in shift of a silver ion, for example, the concern over use of silver plating which was written in the 4,316,679th item Description of the Germany Request for a Patent is conquered, that is because it became clear that shift of silver was prevented substantially, when this invention gives the barrier to moisture.
[0058]As for an immersion-plating constituent, in two modes of the above of this invention, it is preferred to contain the complexing agent to the ion of metal with the higher degree of electropositive.
[0059]The ion of the metal with the higher degree of electropositive in another mode of this invention, As a result of making the aquosity plating constituent containing the antitarnish agent for the complexing agent to such ion, and metal with the higher degree of electropositive contact, by forming the coat of metal with the higher degree of electropositive, The substitution metal plating method which plates metal with the low degree of electropositive with metal with the high degree of electropositive relatively is provided.
[0060]the ion of the metal which can perform substitution plating in this mode of this invention -- as compared with this metal ion, it exists in many quantity from an equimolecular amount preferably. The new plating constituent which does not contain substantially the reducing agent which can return this ion to this metal is also provided by containing the complexing agent to this ion and containing the antitarnish agent for this metal.
[0061]It was found out that this mode of this invention is useful for especially plating by silver or bismuth. Therefore, as for the indicated plating constituent, it is preferred to contain the ion of silver or bismuth.
[0062]The plating constituent used for this mode of this invention may be an immersion-plating constituent also based on what kind of plating constituent used for PCB industry.
[0063]In this embodiment of this invention, preferably, before contacting a surface of metal to a plating constituent in a plating stage, a surface of metal is purified. Purification may be using what kind of publicly known purification constituent, acid purification constituent, for example, this technology. An example is PC1144 which is a regulator of the copper which AlphaMetals Limited supplies.
[0064]When the purification stage using acid purification liquid exists, before contacting a surface of metal in plating liquid, generally a cleaning step will exist.

[0065]Preferably, the stage before any purification will include a gloss etching stage.
[0066]When a plating constituent contains a complexing agent, 10-100g/l. 2-200g/l. exists in the quantity around 50g/l. especially most preferably preferably 0.1-250g/l. preferably. A complexing agent may be what kind of complexing agent to the metal ion to plate which does not form insoluble precipitation in water under the aquosity of a constituent, and the conditions of pH. The mixture of a complexing agent may be used. It is desirable to use the complexing agent which is a ligand of two seats or the higher number of seats, and that is because the stability constant of such a complex is higher than a unidentate ligand.
[0067]As an example of a suitable complexing agent, an oxygen content ligand, for example, the amino acid which has two or more piece ten or less carbon atoms preferably, and those salts, polycarboxylic acid -- usually -- aminoacetic acid, for example, nitrilotriacetic acid,. Usually Or ethylenediaminetetraacetic acid (EDTA), a diethylenetriamine pentaacetic acid, N - hydroxyethyl -- ethylenediamine -- triacetic acid -- 1,3 - diamino- -- 2-propanol -- N -- N -- N -- ' -- N -- ' - a tetraacetic acid. The alkylene polyamine polyacetic acid which includes screw hydroxyphenyl ethylenediamine diacetate, a diaminocyclohexane tetraacetic acid, or ethylene glycol bis- [(beta-aminoethyl ether) -N,N'-tetraacetic acid], And N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine, There are citrate and/or a tartrate, a N,N-di-(hydroxyethyl) glycine, gluconate, a lactate, citrate, a tartrate, crown ether, and/or cryptand.
[0068]Especially suitable complexing agents are EDTA, DTPA, and N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine to silver. a complexing agent -- the bottom of the conditions of the pH of plating liquid -- plating -- public funds -- the complex of fusibility must be formed in solution with group ion.
[0069]A complexing agent suitable for bismuth is a chloride, and, generally it is unnecessary to use the complexing agent of a multi-seat ligand (namely, two seats or the higher number of seats) to bismuth.
[0070]As for a complexing agent, it is preferred to use by a stoichiometrical equivalent or an excessive amount of stoichiometrical either so that all the metal ion for plating may be complexed. Stoichiometric shall mean the number of equimolars. a complexing agent exists with molar concentration higher than a silver ion preferably -- a mole ratio -- desirable -- :(at least 1.2) 1 -- more -- desirable -- :(at least 2.0) 1 -- it is :(at least 3) 1 still more preferably.
[0071]As an antitarnish agent suitable for using in all respects of this invention, some are following, for example. : [0072]Preferably (a) Six or more carbon atoms, the carbon atom which is ten or more pieces most preferably, Generally, are 30 or less carbon atoms fatty acid amine which it has, and The first class, They may be the second class, the third class, diamine, amine salt, amide, ethoxylation amine, ethoxylation diamine, quarternary ammonium salt, quaternary 2 ammonium salt, ethoxylation quarternary ammonium salt, ethoxylation amide, and an amine oxidation thing. The example of corrosion inhibitor of the first class, the second

class, and tertiary-amine form is ARMEENtm (tm expresses a trademark). The example of corrosion inhibitor of the amine form following it, respectively DUOMEENtm, ARMACtm/DUOMAC, ARMIDtm, ETHOMEENtm, It is ETHODUOMEENtm, ARQUADtm, DUOQUADtm, ETHOQUADtm, ETHOMIDtm, and AROMOXtm, and all are supplied by Akzo Chemie.

[0073](b) A pudding and a substitution pudding.

[0074](c) The product of the range of SARKOSYL which N-acyl derivative, for example, Ciba-Geigy, of a sarcosine supply.

[0075](d) Organic polycarboxylic acid like Reocor 190 which Ciba-Geigy supplies.

[0076](e) Substitution imidazoline whose substituent is a hydroxy C_1 - C_4 alkylamino group or a basis containing carbonyl, for example. Especially as an example, there is AMINE 0 which was combined with N-acyl sarcosine of the category of (c) and which Ciba-Geigy manufactures.

[0077](f) An alkyl group is 22 or less carbon atoms, the alkyl which have 11 or less carbon atoms preferably and by which alkyl or benzyl is replaced by the case, or alkyl benzylimidazole, for example, undecylimidazole.

[0078](g) an alkyl group -- 22 or less carbon atoms -- preferably ten or less carbon atoms, [have and] Benzimidazole by which alkyl or benzyl is replaced by the case, especially alkyl aryl benzimidazole, especially suitable 2-(p-chlorobenzyl) benzimidazole

[0079](h) Phosphoric ester like EMCOL PS-413 which Witco supplies.

[0080](i) The triazole derivative replaced by a case like REOMET 42 which Ciba-Geigy supplies. Benzotriazol, tollyltriazole, and the number of carbon atoms of an example of an alkyl group are 1-22, and an alkylation triazole derivative that are 1-10 preferably.

[0081](j) Substitution tetrazole, for example, 5 (3 (trifluoro methylphenyl)) tetrazole, is a suitable example.

[0082]although it seems that until dependence of the selection of an antitarnish agent is carried out to some extent at the metal of a surface of metal plated, probably, this will be clear to a person skilled in the art. For example, if it tries to build an antitarnish agent into a golden plating bath, an antitarnish agent may be a salt of a chloride, but by contrast, if a silver plating bath is used, since formation of precipitation of insoluble silver chloride will be caused, don't use the salt of a chloride.

[0083]As for an antitarnish agent, it is preferred that it is water solubility so that a solution may turn into solution. However, although the antitarnish agent which is not mixed with water may be used, it is sometimes required for a solution to include a surface-active agent / assistant solvent.

[0084]as a result of giving ****** in few to that this invention prevents discoloration with the manufactured bare board, and gives the tolerance over humidity, it became clear that the

further protection was given between a bare board manufacturing stage and a part attachment stage. It is found out that soldering fitness is enhanced.

[0085]Although pH suitable for a silver plating constituent may be 2-12, it is 4-10 preferably. Therefore, a constituent may be the acidity to pH 7. Or a constituent may be alkaline, it may be larger than 7, or may be clear from 7.5, and may have large pH again. The plating liquid of bismuth usually has 1 or low pH not more than it.

[0086]A buffer may be included in a plating constituent and it may secure that pH of a constituent is in request within the limits. As a buffer, what kind of acid or base which can suit may be included. Acid or the base which can suit is acid or the base which does not produce precipitation from the solution of a silver ion and/, or a complexing agent in the quantity needed for a constituent. For example, hydrogen chloride is unsuitable to a silver plating constituent in order to form precipitation of insoluble silver chloride. As a suitable example, there is hydroxide or carbonate of sodium or potassium, or when acid is required, there may be citrate, nitric acid, or acetic acid as suitable acid. Although borate salt, phthalate, acetate, and an phosphate may be used, it is preferred for a buffer not to produce a precipitate of metal salt and not to stop a plating rate. It will depend for the suitable buffer on desired work pH.

[0087]A plating constituent may contain arbitrary ingredients like a surface-active agent or a wetting agent, in order to improve the homogeneity of a coat. When it includes a surface-active agent, it is preferred to introduce into a constituent in quantity which exists by the concentration of 0.02-100g/l. in a plating bath. desirable -- the concentration of 0.1-25g/l. -- it will incorporate by the concentration of 1-15g/l. most preferably. What kind of standard surface-active agent or wetting agent which is useful for a plating bath may be used. A nonionic surface active agent is preferred. Especially a suitable surface-active agent, respectively *Synperonic NP9 (ICI), * They are alkylphenol ethoxy RATO like [Harcros] Synperonic A14 (ICI) and *EthylanHB4, alcoholic ethoxy RATO, and phenol ethoxy RATO (* shows a trade name).

[0088]Another arbitrary ingredient included in the plating bath of this invention is a grain-refining agent. A grain-refining agent improves the appearance of the plated surface of metal by making the smaller crystal of the metal which has the structure with which high density was filled up more and which is plated form. As a suitable example of a grain-refining agent, there are lower alcohol (for example, isopropanol), for example, the lower alcohol which has 1-6 carbon atoms, and a polyethylene glycol (Carbowax* and Union Carbide), for example, PEG 1450. A grain-refining agent may be included in a constituent in the quantity of 0.02-200g/l. a grain-refining agent is included more preferably -- if it becomes, I will come out [in / most preferably / 0.05-100g/l. / the concentration of 0.1-10g/l.]. what kind of non-aqueous solvent -- a constituent -- less than 50 weight % must exist in the amount of things preferably 10 of less than 30 weight % or a plating constituent, or less than 5weight %.

[0089]The inactive noninterferential nature ingredient of others, such as a defoaming agent (for example, A100 which Dow supplies) for a spraying cloth, and a color, may be included especially.

[0090]The emainder of a constituent is water. Deionized water or other pure water from which the ion of coherence was removed is used for the plating constituent used for the method of this invention.

[0091]In order to form the plating constituent used for the method of this invention, The solution which contains a complexing agent as it was defined as deionized water and the above with other arbitrary ingredients by the case, and any buffers preferably is prepared first, and the salt of metal with the higher degree of electropositive is added to the ingredient of others which were formed in what carried out preliminary mixing as solution. Although it has become clear that it is the most convenient method of preparing a solution, this, It takes time comparatively that it is going to dissolve a metaled salt in a plating constituent directly, and that is because there is a tendency which is easier to produce the photoreaction which causes the precipitation as dark precipitation of the silver ion from a solution, when metal is silver.

[0092]Probably as for pH of the constituent which is going to add a silver salt, pH 3-10 will be preferred, and it will be 4-8 most preferably.

[0093]An ingredient is mixed until they will dissolve substantially. Use of the heat for the dissolution of silver is inconvenient from there being a tendency to make precipitation of dark silver form too.

[0094]After contact with the solution and bare board containing an antitarnish agent dries a board. A washing latter-part story is made to exist between contact with a solution and a board, and desiccation preferably.

[0095]By any means, although desiccation is good, it is using warm air, for example, generally, may pass the oven for desiccation for the processed metal.

[0096]The surface the coat obtained using the method of this invention is more remarkable than what was obtained by the conventional HAL method, and homogeneous [a coat], and flat is formed, and a coat is more tolerant to soldering operation as compared with protection of the quality of organicity. The method of this invention is cheap and easier than use of the method of nickel/gold.

[0097]In a subsequent part attachment stage, parts are soldered to the pad and/or run through hole with which the bare board was plated. It may tend to mix the metal (generally copper) of a pad and/or a run through hole, the metal (it is usually silver) to plate and/, or each other's metal and solder to plate. The formed combination with parts has good electrical conductivity and good bonding strength.

[0098]The finished board with which after part attachment covered the layer with which this invention was plated, and parts were attached is not afflicted by the problem of the reliability of

combination whose board formed using the stage of nickel/gold is so.
[0099]
[Working example]
Working example 1[0100]The constituent which mixed EDTA50g and 20.4 g of solid sodium hydroxide with sufficient water to dissolve them was prepared. Then, in addition to the reserve mixture which contains EDTA and a sodium hydroxide solution for the solution which contains the silver nitrate 1g in deionized water, deionized water was added and it was made 1 l. The double-sided circuit board of the copper which has various surface mounting feature objects and the run through hole with which various diameters were plated was coated with the silver solution using the following procedure.
[0101]Gloss was chemically given to the board for 1 minute in H_2O_2 (35%), H_2SO_4 (96%) of 0.5 volume %, and 2.5% of solution of 1,4-butanediol of 20 volume %. Subsequently, pickling was carried out for 1 minute in 10%H_2SO_4 after that using washing by tap water. It rinsed to the board once again, it ranked second to it, and was immersed in silver plating liquid for 4 minutes at 40 **. The board was rinsed and dried by warm air after taking out from a bath. The region of copper of a board was coated with the glossy flat silver sludge.
[0102]Give the covered board to three paths which pass the reflow characteristic image of typical IR soldering paste (drawing 1 in which an example with a suitable temperature over the time about a reflow path is shown should be referred to), and it ranks second, Wave soldering was carried out using the no clean fusing agent which does not contain VOC (volatile organic compound) of Alpha Metals Limited called NR300. 100% of restoration by the solder of the plated run through hole was attained.
[0103]After storing a board by 40 **/93% of RH (relative humidity) in a humid cabinet for 24 hours, 3 times of IR reflow characteristic images were passed. These boards showed slight discoloration on the silver film. However, 100% of restoration of the hole was too attained between wave soldering of after that by the fusing agent of NR300.
[0104]Working example 2[0105]Silver plating liquid was prepared by forming the solution containing EDTA50g, NaOH20.4g, Ethylan HB4(Akros Chemicals)14g, and Crodamet02 (CrodaChemicals)3g into 800 ml of deionized water. The $AgNO_3$1g solution in 100 ml of deionized water was added to this solution. By addition of rare NaOH/HNO_3, it adjusted to 6.8, and it ranked second and pH was 1 l. using deionized water.
[0106]The copper double-sided bare board was coated with the above-mentioned solution using the procedure of a description in the working example 1. After passing 3 times of IR reflow characteristic images, 100% of restoration with the solder of the run through hole plated on the occasion of wave soldering by the fusing agent of NR300 was attained.
[0107]Before passing 3 times of IR reflow characteristic images, the board stored by 40 **/93%

of RH for 24 hours did not show the proof of discoloration at all, but was fully soldered on the occasion of a wave soldering examination, and 100% of restoration of the hole was made.
[0108]Working example 3[0109]The copper double-sided bare board was coated using the bath constituent and procedure of a description in the working example 1. After taking out and washing a board from silver plating liquid, it was immersed in the solution (pH 7) in Reomet42 (Ciba-Geigy) 4 g of deionized water [1 l. of] for 1 minute at the room temperature. Subsequently, the board was washed and dried by warm air with tap water. The glossy flat silver film was formed.
[0110]The painted board is stored by 40 **/93% of RH for 24 hours, it ranked second and the reflow characteristic image of three IR pastes was passed. The board was fully soldered, when proof of discoloration was not shown at all but wave soldering was carried out using the fusing agent of NR300.
[0111]Working example 4[0112]The strip-of-paper-like copper coupon (5 cm x 1 cm) was coated with the silver film in the working example 2 as the description. In addition, some samples were coated using immersion tin coating, the coating by Sn/Pb of 63/37, and the soldering fitness preservation coating by two kinds of competition substances based on the chemistry of substitution benzimidazole. The following coating procedure was applied to various samples. : [0113]Immersion tin coating[0114]The coupon was etched for 2 minutes in the solution of $Na_2S_2O_8$ (5%) and H_2SO_4 (5%), and tap water washed it, subsequently it was washed for 1 minute by 10% of H_2SO_4, and, subsequently was washed by deionized water. A coupon in deionized water Subsequently, 33g/l. $Sn(BF_4)_2$, 150g/l. of thiourea, a 20g/l. fluoroboric acid, and 5g/l. Synperonic NP9 were immersed in the immersion tinning liquid included from ICI for 1 minute at the room temperature. Subsequently, the coupon was washed and dried by warm air by deionized water.
[0115]Sn/Pb coating[0116]etching a coupon in the solution containing $Na_2S_2O_8$ (5%) and H_2SO_4 (5%) -- tap water -- subsequently -- 10% of H_2SO_4 -- subsequently it washed by deionized water. The coupon was dried by warm air. Subsequently, a fusing agent called NR300 of Alpha was applied to each coupon. Subsequently, the coupon was coated by immersion for 3 seconds at 250 ** to melting solder at 63/37 of Sn/Pb.
[0117]The azole 1 and azole 2[0118]The coupon was etched and washed to the passage about the sample of immersion tin. Subsequently, the coupon was immersed in the solution containing azole for 90 seconds at 40 **. After taking out from an azole content solution, the coupon was washed and dried by warm air by deionized water.
[0119]The coupon was given to various kinds of different pretreatments.
[0120]A. Pretreatment is completely nothing.
[0121]B. The reflow characteristic image by 3 times of soldering paste is passed.

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皮　膜	前　処　理	湿潤時間／秒	湿潤力／2秒
実施例2	A	0.7	0. 29
実施例2	B	0.8	0.444
実施例2	C	0.7	0.429
実施例2	D	0.7	0.441
実施例2	E	0.8	0.438
ス　ズ	A	0.9	0.488
ス　ズ	B	>5	−0.028
ス　ズ	C	>5	0.008
ス　ズ	D	>5	−0.148
アゾール1	A	0.8	0.439
アゾール1	B	0.9	0.412
アゾール1	C	0.9	0.443
アゾール1	D	0.9	0.426
アゾール1	E	1.0	0.421
アゾール2	A	0.9	0.449
アゾール2	B	1.0	0.417
アゾール2	C	0.9	0.466
アゾール2	D	1.1	0.310
アゾール2	E	1.2	0.296
Sn／Pb	A	0.8	0.475
Sn／Pb	B	0.8	0.501
Sn／Pb	C	0.8	0.492
Sn／Pb	D	0.8	0.474
Sn／Pb	E	0.8	0.492

[0129]The silver film prepared according to this invention has humid time shorter than the alternative plan of Sn and benzimidazole, and high wetting power, and after processing of humidity and heat holds these characteristics more easily as he can understand from the above.

[0130]Working example 5[0131]The bismuth oxide 3.9g, 183.1 g (as a 37% solution) of hydrogen chloride, The glycolic acid 490.5g (70% solution) and 265.4g (50% sodium hydroxide solution), preparing the substitution bismuth plating constituent containing 0.077 g of potassium iodide, Synperonic NP9(ICI)0.003g, and 4 g of 2p-chlorobenzylbenzimidazole -- deionized water -- in addition, 1 l. of product solutions were produced. Gloss was chemically given to the working example 1 as the description, and it ranked second to the bare board which has a copper pad and a copper run through hole, and was immersed in the plating bath for 2 minutes at 70 **. On the surface of copper, the coat of the bismuth which has the

thickness of 0.05 micrometer was formed. The examination of subsequent soldering fitness and color fastness carried out to the plated bare board showed the result good about soldering fitness and color fastness.

[0132]Working example 6[0133]Gloss etching of the copper double-sided bare board was carried out for 1 minute at the room temperature in HNO_3, 10% of H_2SO_4, 10% of H_3PO_4, and 1% of solution of HCl of 50 volume %. Subsequently, tap water washed the board and it washed for 1 minute by 10% of H_2SO_4 after that. After rinsing once again, the board was immersed in the silver plating bath given in the working example 2 for 4 minutes at 45 **. Subsequently, the board was rinsed and dried by warm air.

[0134]The painted board was stored by 40 **/93% of RH for 24 hours, and the reflow characteristic image by IR paste was passed 3 times. The board was fully soldered, when proof of discoloration was not shown at all but wave soldering was carried out using NR300 fusing agent.

[0135]Working example 7[0136]The diethylenetriamine pentaacetic acid 64.8g, NaOH23.0g, Ethylan HB4(Akros Chemicals)14g that is a surface-active agent, The silver plating bath was prepared by forming the solution which contains 2.5 g of ethoxylation tertiary-amine compounds (Croda Chemicals) called Crodamet 02 in 800 ml of deionized water. The solution of the silver nitrate 1g in 100 ml of deionized water was added to this solution. Addition of a rare NaOH solution or nitric acid adjusted the pH of this solution to 6.9. Subsequently, capacity was 1 l. using deionized water.

[0137]The copper double-sided bare board was coated using the above-mentioned solution using the procedure of a description in the working example 1. After passing 3 times of IR reflow characteristic images, in the case of wave soldering of the painted board using NR300 fusing agent of Alpha Metals. 100% of restoration of the plated run through hole was attained, and proof of discoloration was not shown at all, but it was fully soldered on the occasion of a wave examination, and 100% of restoration of the hole was performed.

[0138]Working example 8[0139]The immersion silver plating liquid containing 98.2 g of deionized water, the nitric acid 1g, the silver nitrate 0.1g, Chemeen C2(antitarnish agent)0.3g, and Mazawet DF(solubilizing agent)0.4g was prepared. pH was adjusted to six using the 50% solution of ethylenediamine. This bath formed the adhesive silver sludge on the copper coupon, and showed good soldering fitness and moisture resistance.

[0140]Working example 9[0141]2.1weight % of a bismuth trioxide, 46.73weight % of chloride (22 degrees Baume), The bismuth plating liquid containing the distilled water of 2 or 1.2 weight % of Chemax ChemeenC of 49.5weight % of glycolic acid (70%), 0.07weight % of potassium chloride, and 0.1weight % of polyethylene glycols [600 or 0.2 weight % of] and 0.1weight % of tartaric acid was prepared. Another solution from which Chemeen C2 was removed was prepared. The sample of copper coating printed circuit material was plated in each solution.

Subsequently, these plated samples were put on the moistness room of 60 ** and 95% relative humidity for 16 hours.

[0142]What was prepared in the solution which inspects a sample after this exposure and does not contain Chemeen C2 was discolored violently. The sample prepared in the solution containing an antitarnish agent showed a good soldering possibility, when the good appearance by the minimum oxidation was had and examined.

[Translation done.]

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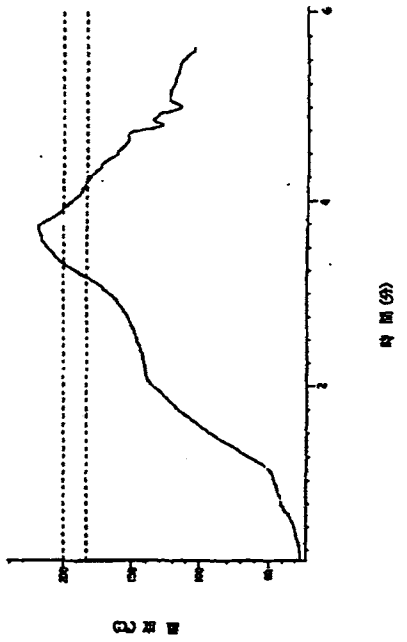
(54)【発明の名称】　プリント回路板の製造

(57)【要約】
【課題】　ＰＣＢの製造の際に用いられる方法は、金属のパッドおよび／または通し穴を保護して、耐変色性の、はんだ付けできる皮膜を与えることを含む。
【解決手段】　この方法では、好ましくは浸漬法によって、パッドおよび／または通し穴を光沢食刻し、金属めっきし、そして変色防止剤で処理する。変色防止剤を浸漬めっき浴に組み込んでもよい。金属めっきは、通常、銀またはビスマスを用いて行われ、パッドおよび／または通し穴は銅を含む。



【特許請求の範囲】

【請求項１】　金属のパッドおよび／または通し穴とともに絶縁層および導電層を含むＰＣＢを塗装し、ここで、該パッドおよび／または通し穴に変色防止剤の皮膜を与える方法であって、光沢食刻の段階で、該パッドおよび／または通し穴を光沢食刻組成物に接触させること；ならびに、その後、はんだ付けできるめっきされた金属表面を形成する浸漬金属めっき段階で、該パッドおよび／または通し穴を形成する金属より電気的陽性度が高い金属のイオンを含み、該イオンに対する還元剤を実質的に含まない、めっき組成物に接触させることによって、食刻されたパッドおよび／または通し穴を金属めっきすることを含む方法。

【請求項２】　めっきした金属の表面を変色防止剤の溶液に接触させる請求項１記載の方法。

【請求項３】　金属のパッドおよび／または通し穴とともに絶縁層および導電層を含むＰＣＢを塗装し、ここで、該パッドおよび／または通し穴に変色防止剤の皮膜を与える方法であって、はんだ付けできるめっきされた金属表面を形成する金属めっき段階で、めっき組成物に接触させることによって、食刻されたパッドおよび／または通し穴を金属めっきし、そしてめっきされた金属表面を変色防止剤の溶液に接触させることを含む方法。

【請求項４】　金属めっき段階が、該パッドおよび／または通し穴の金属より電気的陽性度が高い金属を、より電気的陽性度が高い該金属のイオンを含有し、該イオンに対する還元剤を実質的に含まない水溶液から浸漬／置換塗装する方法である請求項３記載の方法。

【請求項５】　めっき組成物が、該イオンに対する錯化剤、好ましくは多座配位子錯化剤を含有する請求項１～４のいずれか一項に記載の方法。

【請求項６】　めっき組成物が変色防止剤を含み、該方法において、めっき段階の際に、変色防止剤が金属めっき組成物中に存在するように、変色防止剤を含む溶液に金属表面を接触させる請求項２～４のいずれか一項に記載の方法。

【請求項７】　めっき段階で金属めっきされた表面を形成し、その後、洗浄後の第二の段階で、変色防止剤を含む溶液に形成済みのめっきされた金属表面を接触させる請求項２～４のいずれか一項に記載の方法。

【請求項８】　変色防止剤を含む溶液とめっきされた金属表面との接触時間が１０秒～５分である請求項２～４、６または７のいずれか一項に記載の方法。

【請求項９】　浸漬塗装または吹付け塗装によって、変色防止剤を含む溶液に金属表面を接触させる請求項２～４および６～８のいずれか一項に記載の方法。

【請求項１０】　変色防止剤が、溶液の０．００１～５重量％の量で該溶液中に存在する請求項２～４および６～９のいずれか一項に記載の方法。

【請求項１１】　めっきされた金属表面の金属の皮膜が、ニッケル、銀、スズ、鉛、パラジウム、コバルト、金、白金もしくはビスマス、またはそれらの合金、好ましくは銀を含む請求項１～１０のいずれか一項に記載の方法。

【請求項１２】　パッドまたは通し穴が銅で形成されている請求項１～１１のいずれか一項に記載の方法。

【請求項１３】　ＰＣＢの表面に露出した導体の痕跡に絶縁体であるマスクを、パッドおよび／または通し穴が露出したままとなるように施す予備的段階を含む請求項１～１２のいずれか一項に記載の方法。

【請求項１４】　金属めっきと直接接触するはんだを用いて、金属めっきしたパッドおよび／または通し穴に導電性部品を取り付ける後続段階を含む請求項１～１３のいずれか一項に記載の方法。

【請求項１５】　電気的陽性度が比較的低い金属の下地に電気的陽性度が比較的高い金属の浸漬めっきを形成するのに適した水性めっき組成物であって、より電気的陽性度が高い金属のイオン、および該イオンに対する錯化剤、ならびに、より電気的陽性度が高い該金属に対する変色防止剤を含有し、そして該イオンに対する還元剤を実質的に含まない組成物。

【請求項１６】　変色防止剤が、組成物の０．００１～５重量％の量で溶液中に存在する請求項１５記載の組成物。

【請求項１７】　該イオンが、ニッケル、銀、スズ、鉛、パラジウム、コバルト、金、白金もしくはビスマス、またはそれらの合金、好ましくは銀のイオンである請求項１５または１６に記載の組成物。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】プリント回路板（ＰＣＢ）の製造の際は、第一の（多段階）段階で「裸板」を作製し、第二の（多段階）段階で、その板に様々な部品を取り付ける。本発明は、第二の製造段階へと進む前に保護層で裸板を被覆する、裸板の製造における最終段階に関する。

【０００２】

【従来の技術】第二段階で部品を裸板に取り付けるためには、現在２形式の部品：すなわち、有脚部品、例えば抵抗器、トランジスタ等、および、より最近の、表面据付けデバイスがある。有脚部品は、脚のそれぞれを板の穴に通し、次いで、脚の周囲の穴がはんだで満たされることを確保することによって、板に取り付ける。表面据付けデバイスは、平坦な接触部域でのはんだ付け、または接着剤を用いた接着によって、板の表面に取り付ける。

【０００３】第一の段階では、絶縁層、導電性の回路図形、ならびに導電性のパッドおよび／または通し穴を含む板を製造する。板は、複数の導電性回路図形を絶縁層の間に配置した多層の板であってよく、あるいは１層の

絶縁層および１個の導電性回路図形を含んでもよい。

【０００４】通し穴は、それらが導電性であるように、そしてその後の部品取付け段階で表面据付け部品か取り付けられる部域を形成するパッドも導電性であるように、通しめっきしてよい。

【０００５】回路図形、パッドおよび通し穴の導電性部域は、いかなる導電性材料、または異なる導電性材料の混合物で形成してもよいが、一般的には銅で形成する。経時的に、銅は酸化して、劣悪なはんだ付け適性を有する酸化銅の層を形成する傾向があることから、第二の部品取付け段階へと進める前に、はんだ付け適性を保持して、はんだ付けができにくい酸化銅の表面層の形成を防ぐことが望ましい、パッドおよび／または通し穴の部域を覆って保護層を塗装する。

【０００６】裸板を作製するには、複数の方法があるが、裸板の作製に最も広く用いられる方法の一つは、「裸銅を覆うはんだマスク」（ＳＭＯＢＣ）の手法として公知である。そのような板は、一般に、導電性材料で片面または両面を被覆したエポキシ結合ファイバーグラスを含む。一般に、この板は、回路図形を含む導電層と絶縁層とを交互に有する多層板であると思われる。導電性材料は、一般的には金属箔、最も普通には銅箔である。ＳＭＯＢＣ手法では、そのような板を入手し、テンプレートまたは自動化ボール盤を用いて、板材を穿孔する。次いで、板全体：すなわち箔の上面と通し穴の表面との双方に銅の層を析出する無電解銅めっき法を用いて、穴を「通しめっき」する。

【０００７】次いで、板材を感光性薄膜（フォトレジスト）で被覆し、予め選ばれた部域で露光させ、化学的に現像して、露光させなかった部域を除去して、めっきされた通し穴およびパッドである導電性部域を露出させる。一般的には、次の段階で、もう一つの銅の電気めっき段階によって、露出した部域の金属箔の肉厚を増加させる。普通はスズ－鉛合金の電気めっき組成物である、食刻レジストの保護層を露出させ、増厚した銅の部域を覆って施す。

【０００８】次いで、フォトレジストを除去して、除去するための銅を露出させ、銅エッチング組成物を用いて、露出した銅の表面を食刻して除去し、最終的に必要とされる回路図形に銅を残す。

【０００９】次の段階では、スズ－鉛合金のレジストを剥ぎ取る。

【００１０】銅の回路痕跡には部品を取り付けないことになるため、一般的には、痕跡ではなく通し穴およびパッドに部品を取り付けるのに、はんだを塗装することのみが必要とされるにすぎない。したがって、例えばスクリーン印刷法、または光結像に続く現像および、場合により、硬化の手法を用いて、はんだマスクを板に施して、はんだ塗装を必要としない部域を保護する。次いで、穴およびパッドの露出した銅を浄化し、はんだ塗装のために準備し、その後、例えば、はんだ浴への浸漬に続く熱風平滑化（ＨＡＬ）によって、保護はんだ皮膜を塗装して、銅の、はんだマスクで被覆されていない部域に保護はんだ皮膜を形成する。はんだは、はんだマスクを濡らさないため、はんだマスクで保護された部域の上端には、皮膜が全く形成されない。

【００１１】この段階で、板は、少なくとも１層の絶縁層および少なくとも１層の導電層を含む。単数または複数の導電層は、回路痕跡を含む。板は、はんだの層によって変色から保護された単数または複数のパッドおよび／もしくは通し穴も含む。単一の導電層は、回路痕跡もしくはパッドのいずれか、または双方を含んでよい。いかなるパッドも、多層板の外層である導電層の一部となるであろう。板上の回路痕跡は、はんだマスクで被覆する。

【００１２】そのような板は、部品の取付けのための第二段階へと直ちに進め得る。この第二段階では、一般に、はんだを用いて部品の取付けを達成する：すなわち、初めに、一般的には印刷によって、１層のはんだペースト（はんだおよび融剤を含む）を板に塗布し、印刷された板に部品を配置する。次いで、オーブン内で板を加熱して、はんだペースト中のはんだの融合を生起し、それが部品と板との接点を形成する。この方法は、リフローはんだ付けとして公知である。これに代えて、溶融はんだ浴越しに板を通過させるウェーブはんだ付け法も用いられる。いずれの場合も、いかなる保護はんだ皮膜にも重ねて、追加のはんだを用いる。

【００１３】有脚部品と表面取付けデバイスの双方の追加的な複雑化、および多くの密集した小部品を取り付ける特殊な必要性は、ＰＣＢ上の、部品を取り付けようとする導電性金属のための表面保護皮膜に対する増大した要求を招いている。裸板製造業者が施す仕上げは、平坦でない表面を有するパッドを、それが電気的故障の危険性を増大させることから、残さないことが不可欠である。保護皮膜がその後のはんだ段階に干渉し、それによって、裸板と部品との良好な導電性結合の形成を妨げることがないことも不可欠である。保護皮膜を除去する余分な段階は、望ましくないであろう。

【００１４】上記に説明したとおり、導電性金属表面は、一般的には、銅で形成し、保護表面を第一段階の終点で施して、部品取付け以前の、銅表面でのはんだ付けできない酸化銅の形成を防止しなければならない。これは特に重要であるが、それは、第一段階と第二の、部品取付け段階とは、概して、完全に異なる部所で実施されると思われるからである。そのため、導電性のパッドおよび／または通し穴の形成と部品取付け段階との間には、少なからぬ時間的遅延が存在することがあり、その間に、酸化が発生することがある。したがって、導電性材料のはんだ付け適性を維持し、裸板に部品を取り付けたときに、はんだ付けされた接点が形成されるのを可能

にすると思われる保護皮膜が必要とされる。

【００１５】現在用いられている最も一般的な保護皮膜は、その一例を上記に詳述した「ＨＡＬ」（熱風平滑化）法を用いて一般的に施されるスズ／鉛はんだである。

【００１６】ＨＡＬ法は、はんだを均等に施すのが困難であり、ＨＡＬ法の使用によって形成される肉厚分布が、現在用いられている非常に小型の密集した部品を信頼できるように取り付けるのを困難にすることから、限度がある。

【００１７】ＨＡＬによるはんだ層の塗装に対するいくつかの代替処理が紹介されている。皮膜は、部品との信頼できる電気的接点の形成を可能にしなければならない。また、多段階のはんだ付けに耐えられなければならない。例えば、上記のとおり、裸板に取り付けるのに、現在、有脚部品と表面取付け部品の両者が存在し、一般的には、少なくとも２回のはんだ付け操作で取り付けられるものと思われる。したがって、第二の操作ではんだ付けしようとする部域が、第一の操作の際に保護されて残るよう、保護皮膜は少なくとも２回のはんだ付け操作にも耐えられなければならない。

【００１８】ＨＡＬ法に用いられるスズ／鉛合金のはんだに対して提案されている代替策としては、有機的保護、浸漬スズまたはスズ／鉛めっき、およびニッケル／金めっきがある。ニッケル／金の方法では、ニッケルのプライマー層を銅に塗装し、その後、金の層を塗装する、銅表面の無電解めっきを実施する。この方法は、多くの工程段階が存在し、その上、金の使用は高価な工程を招くことから、不都合である。

【００１９】はんだ付けの前の貯蔵および組立の際の、銅パッドに対する有機的保護も、融剤のラッカーを用いて実施されている。その使用は、一般に、片面の板（すなわち、一方の面にのみ導電性パッドを有する板）に限定されている。皮膜は、一般に、浸漬、吹付けまたはローラー塗装によって施される。不幸にも、板の表面に堅実な皮膜を与えるのが困難なため、皮膜の多孔性、およびその堅実でない皮膜の肉厚に起因して、限定された期待寿命を招く。融剤ラッカーも、比較的短い棚保ちを有することが判明している。もう一つの問題は、部品取付け段階で、部品を取り付けるのにリフローはんだ付けを用いようとするならば、板の下側の適所に部品を接着剤で固定することである。融剤ラッカーが厚い場合、接着剤は、印刷された板に部品を直接結合するのではなく、代わりに、接着剤とラッカーの皮膜との間に結合を形成する。この結合の強さは、溶融処理およびはんだ付けの段階の際に低下して、はんだ浴との接触の際に部品を脱落させる可能性がある。

【００２０】現在用いられているもう一つの代替策は、銅表面に銅錯体化合物を形成するイミダゾールまたはトリアゾールの使用に基づく、不動態化／保護処理である。したがって、これらの皮膜は、表面に化学的に結合し、銅と酸素との反応を防止する。しかし、この方法は、連続するはんだ付けの段階に耐えるのに不適切な傾向があるため、最初のはんだ付け段階で到達する高温がこの層を破壊し、それ以上の部品を取り付けるのに必要な、その後のはんだ付け操作に耐えられない傾向があることから、不都合である。そのような方法の一例がヨーロッパ公開特許第0,428,383 号公報に示されていて、ここには、銅または銅合金の表面処理の方法であって、炭素原子数が少なくとも３のアルキル基を２の位置に有するベンゾイミダゾール化合物、および有機酸を含有する水溶液に銅または銅合金の表面を浸漬することを含む方法が記載されている。

【００２１】

【発明が解決しようとする課題】銀を含む組成物を用いて、皮膜を与える方法も公知である。

【００２２】無電解銀めっき法のための３種類の一般的な錯化系は、アンモニア、チオ硫酸塩、またはシアン化物のいずれかに基づく系である。

【００２３】アンモニア系は、アンモニアを含有する銀の溶液が不安定であり、爆発性のアジ化物が形成される傾向があり得るために、不都合である。チオ硫酸塩系は、形成される銀皮膜中の硫黄化合物が、劣悪なはんだ付け適性を招くため、その後の部品取付け段階で、裸板と部品との間に劣悪な電気的接点が形成されることがあることから、電子工学産業での利用には不都合である。

【００２４】シアン化物に基づく系は、めっき液が有毒であるために、不都合である。

【００２５】米国特許第5,318,621 号明細書には、回路板上の銅を覆うニッケル皮膜に銀または金を析出させる増速剤として、アミノ酸を含有する無電解めっき液が開示されている。チオ硫酸塩／硫酸塩に基づく金または銀の無電解めっき浴は、銅が、銀または金の皮膜を形成させることなく、急速に溶解することから、いずれも銅に直接めっきしないであろうことが記載されている。この引用文献の序論では、「Metal Finishing Guidebook & Directory 」（1993年版）が考察されている。硝酸銀、アンモニア、およびホルムアルデヒドのような還元剤を含む銀めっき液が言及されている。

【００２６】米国特許第4,863,766 号明細書も、シアン化物に基づくめっき液を用いる無電解銀めっきを開示している。Metal Finishing 、第81巻第１号（1983年）27～30ページで、Russevは、硝酸銀および窒素錯化剤を含有するめっき液からの銅粉の浸漬銀めっきを記載している。Metal Finishing ８月号（1960年）53ページで、Geldは、黄銅または銅の下地に最初に光沢浸漬を、次いで、硝酸銀およびヨウ化カリウムの溶液から銀の厚い皮膜をめっきする銀めっき段階を伴う銀の塗装法を記載している。この方法は、電気的接点をめっきして導電率を上昇させるためのものである。

【００２７】特開平4-110474号公報では、母材を銀でめっきし、乾燥し、次いで、メルカプタン化合物で処理して変色を防いでいる。ドイツ国特許願第4,331,679 号明細書では、銅のような卑金属を、パラジウム塩および酸化剤を含有する浴にその表面を接触させる第一段階を含み、第二段階で、パラジウム塩、錯化剤およびギ酸またはギ酸誘導体を含有する浴に接触させる二段階の方法でパラジウムで塗装する。後者の浴は、分解または「めっき切れ」に対して浴を安定させる、浴それ自体のための安定剤を含有してもよい。銅である下地は、過硫酸塩を含有する非光沢食刻浴を用いて、予め食刻しておかなければならないことが示唆されている。しかし、そのような前処理の段階は、比較的多孔性に富む皮膜を形成する傾向がある。本発明者らは、最初の段階で非常に薄い皮膜が形成される二段階の方法を用いて、皮膜の多孔率を最小化する。この参照は、移行を理由として銀を腐食防止に用いることに対する警告となる。

【００２８】

【課題を解決するための手段】本発明は、より電気的陽性度が高い金属が、塗装しようとする表面で、より電気的陽性度が低い金属と置き換わる置換浸漬金属めっきに関する。より電気的陽性度が高い金属のイオンは、下地の金属を酸化する。置換めっき法は、保護しようとする表面の酸化できる金属、および銀イオンのそれぞれの相対電極電位による単純置換反応によって、銀皮膜を金属の表面に形成することから、無電解法とは異なる。

【００２９】例えば、J. Wiley & Sons 社によって発行された、F.A. Lowenheimによる「現代の電気めっき（Modern Electroplating ）」（1963年）では、銀は置換によって、ほとんどの卑金属にめっきするが、浸漬めっきされた銀は、僅かにしか接着性ではないことが報告されている。F.A. Lowenheimは、卑金属を銀で電気めっきするときは、高シアン化物衝撃浴から、最初に銀の薄膜を素材に析出させて、その後の電気めっきされた銀の層の良好な接着を確保することが必要であることを示唆している。

【００３０】本発明は、裸板の製造段階と部品取付け段階との間での変色から保護することが必要な裸板の導電性表面に対する、はんだによる保護塗装に対する代替策を提供することを目的とする。

【００３１】

【発明の実施の形態】本発明によれば、金属のパッドおよび／または通し穴とともに絶縁層および導電層を含むＰＣＢを塗装し、ここで、該パッドおよび／または通し穴に変色防止剤の皮膜を与える方法であって、光沢食刻の段階で、該パッドおよび／または通し穴を光沢食刻組成物に接触させること；ならびに、その後、はんだ付けできるめっきされた金属表面を形成する金属めっき段階で、食刻されたパッドおよび／または通し穴を浸漬めっきすることを含む方法が提供される。

【００３２】ＰＣＢの絶縁層および導電層は、上記のとおりであると思われる。それらは、それぞれ、いかなる慣用のＰＣＢの絶縁層および導電性回路の図形を含んでもよい。めっきするためのパッドおよび／または通し穴は、ＰＣＢの、その後の部品取付けのためのはんだ付け段階で、部品を取り付けるためにはんだ付け適性を維持しなければならない部域である。

【００３３】光沢食刻段階は、パッドおよび／または通し穴を光沢食刻組成物に接触させることを含む。そのような組成物は、当業界では他の用途のために既知であり、パッドおよび／または通し穴が形成される導電性金属に、光沢のある、平滑な、浄化された表面を形成する。対照的に、非光沢食刻組成物、例えば、過硫酸塩に基づく組成物は、微細粗面化された、浄化された表面を与える。光沢食刻段階の利用は、その後のはんだ付け段階に特に適した濃密な、多孔性でない金属皮膜の形成を可能にする。

【００３４】適切な光沢食刻組成物は、一般に水性であり、例えば、過酸化水素、硫酸、硝酸、リン酸または塩酸のうち１種類、またはそれより多くの混合物に基づいてよい。光沢食刻組成物は、一般に、光沢食刻組成物中への銅の溶解を変化させる傾向があると思われる少なくとも１種類の成分を含有する。

【００３５】パッドおよび／または通し穴の金属表面が銅または銅合金を含む、特に好適な光沢食刻組成物は、例えば特開昭62-188785-A2号公報（水溶液中に５．１～１０．２モル／リットルの硝酸、４．６～９．２モル／リットルの硫酸、０．０１モル／リットルの硝酸亜鉛および０．４モル／リットルの硝酸銅を含有）；特開昭60-190582 号公報（例えば２０～５０重量％の硫酸（９６％）、１０～２５重量％の硝酸（６７．５％）、０．５～１重量％の塩酸（３５％）および０．５～１重量％の非イオン界面活性剤を含有）；米国特許第3,668,131 号明細書（過酸化水素、硫酸および尿素添加物を含有）；Metal Finishing 、第84巻第２号（1986年２月）67～70ページ（重クロム酸ナトリウム、硫酸、塩酸、ジエチルジチオ炭酸ナトリウムを含有）；Trans. Inst. Metal Finishing、第61巻第２号（1983年夏）46～49ページ（過酸化水素、硫酸および安定剤を含有する酸性化過酸化水素）；Oberflaeche Surf、第20巻第８号（1979年８月）178 ～179 ページ（硝酸および塩化ドデシルピリジニウムを含有）；米国特許第4,510,018 号明細書（硫酸、過酸化水素、脂肪酸アミンおよびアンモニウム化合物を含有）；米国特許第4,459,216 号明細書（５～１００ｇ／リットルの過酸化水素および１００～３００ｇ／リットルの硫酸ならびに芳香族安定剤を含有）；特開昭59-038308 号公報（０．１５～０．３モル／リットルの塩酸、０．２～０．４モル／リットルのリン酸および０．０２～０．１モル／リットルの硫酸を含有）に記載のとおりである。パッドおよび／または通し穴の導電性材料がス

テンレス鋼を含む場合、特に好適な光沢食刻組成物は、例えば国際公開特許第93-08317号公報；特開昭(62)-238379-A2号公報；ドイツ国公開特許第1,928,307 号公報；またはTr. Gos. Nauchno-Issled. Proektn. Inst. Osnovn. Khim. 、第36巻（1974年）93～97ページに記載のとおりであってよい。導電性材料がアルミニウムである場合、適切な　沢食刻は、Met. Finishing、第84巻第７号（1986年７月）55～59ページに記載のとおりである。

【００３６】したがって、光沢のある、浄化された表面を与えるいかなる食刻組成物を用いてもよい。光沢食刻段階では、光沢食刻組成物との接触は、例えば上記の参照文献のいずれかに記載されたような、光沢のある表面がパッドおよび／または通し穴の導電性材料に形成されるのを可能にするのに充分な時間および適した温度での浸漬、吹付けまたは他のいかなる塗装手法によってもよい。一般に、光沢食刻組成物との接触のための温度は常温であり、接触時間は５秒～１０分、好ましくは３０秒以上、または２分以上でさえあり、好ましくは５分間以下であろう。

【００３７】一般に、食刻段階の後は、裸板を脱イオン水で洗浄することを含み、一般的には乾燥することなく、次いでめっき段階へと直接進める、洗浄後段階が存在することになる。これに代えて、酸洗い段階を水洗後に含ませてもよい。

【００３８】めっき段階は、浸漬（または置換）めっき段階である。

【００３９】浸漬めっき段階では、めっき組成物は、導電性材料より電気的陽性度が高い金属の金属イオンを含む。したがって、浸漬めっき液中の金属イオンの選択は、めっきされようとする金属に依存する。パッドおよび／または通し穴は、一般的には、銅またはニッケルを含むため、めっきする金属の適切な例としては、ビスマス、スズ、パラジウム、銀および金があり；銀およびビスマスイオンが特に好適である。

【００４０】特に好適な浸漬銀めっき法は、参照番号第64/2031/00号のもとに本日出願された、本発明者らの同時係属出願の英国特許出願に記載されている。

【００４１】めっきする金属イオン源としては、いかなる水溶性金属塩、例えば硝酸塩、酢酸塩、硫酸塩、乳酸塩またはギ酸塩を用いてもよい。好ましくは、硝酸銀を用いる。

【００４２】金属めっきするイオンは、一般に、０．０６～３２ｇ／リットル（金属イオンを基準とする）、好ましくは０．１～２５ｇ／リットル、最も好ましくは０．５～１５ｇ／リットルの濃度でめっき組成物中に存在する。めっき液との金属表面の接触は、一般に、１０～９０℃、好ましくは１５～７５℃、より好ましくは２０～６０℃の温度においてであると思われる。例えば、めっき液との接触の温度は、１５～５０℃、最も普通には２０～４０℃であると思われる。

【００４３】接触は、いかなる方法、普通は浸漬、吹付けまたは水平浸漬塗装によることもできる。吹付け塗装が好適である。そのような接触は、実質的に連続する塗装工程の一部であってよい。

【００４４】金属表面とのめっき液の接触時間は、めっきされた金属表面を金属を覆って形成するのに充分である。一般に、接触時間は１０秒～１０分であると思われる。１０秒未満の接触時間は、一般に、銀皮膜による不充分な被覆率を与えることが見出されており、接触時間は１０分より長くてもよいが、１０分より長い接触時間からは、更なる利益が全く見出されていない。

【００４５】好適なめっき法は、浸漬置換法であり、真の無電解めっき法ではない。本発明の好適なめっき組成物中では、溶液中の金属めっきイオンによって、金属の表面の金属原子が酸化される結果、１層のめっきされた金属がパッドおよび／または通し穴上に析出する。この方法は、めっきされた金属が、めっきする金属によって酸化できる金属の表面の部位のすべてを被覆したときには、それ以上の反応、したがってまた、それ以上の析出が全く生じないため、自己限定的である。

【００４６】本発明の第二の態様では、金属のパッドおよび／または通し穴とともに絶縁層および導電層を含むＰＣＢを塗装し、ここで、該パッドおよび／または通し穴に変色防止剤の皮膜を与える方法であって、はんだ付けできるめっきされた金属表面を形成する金属めっき段階で、めっき組成物に接触させることによって、食刻されたパッドおよび／または通し穴を金属めっきし、そしてめっきされた金属表面を変色防止剤の溶液に接触させることを含む方法が提供される。

【００４７】本発明のこの態様では、好ましくは、めっき段階で金属表面をめっき組成物に接触させる前に、金属表面を浄化する。浄化は、酸性の浄化組成物、例えば当技術に公知のいかなる浄化組成物を用いることであってもよい。例は、Alpha Metals Limitedが供給する銅の調整剤であるＰＣ１１４４である。酸性浄化液を用いる浄化段階が存在する場合は、一般に、金属表面をめっき液に接触させる前に、洗浄段階が存在することになる。好ましくは、いかなる浄化前の段階も光沢食刻段階を含むことになる。

【００４８】本発明の双方の態様において、変色防止剤は、めっき液それ自体中に存在してよいため、めっき液は、変色防止剤を含む溶液を含む。したがって、本発明の好適な方法では、めっき段階の際に、めっきされた金属表面を変色防止剤を含む溶液に接触させる（すなわち、接触は、めっきされた金属表面の形成の際であってよい）。

【００４９】あるいは又、めっき段階で金属表面を形成し、その後、形成された金属表面を、もう一つの段階で、変色防止剤を含む溶液に接触させる。溶液は、好ましくは水性であり、脱イオン水か、さもなければ純水か

ら製造される。変色防止剤を含む組成物は、安定剤、例えば非水性溶媒、界面活性剤および／またはpH緩衝剤を追加的に含んでよい。

【００５０】変色防止剤を含む組成物とめっきされた金属表面との接触は、少なくとも５秒間、好ましくは少なくとも２０秒間であろう。めっき液中に変色防止剤が存在する場合、接触の時間は、一般に、めっき段階の持続時間によって決定される。一般的には、接触時間は１～５分であろう。接触の温度は、最も普通には１０～９０℃、好ましくは１５～７５℃、より好ましくは２０～６０℃である。例えば、めっき液との接触の温度は、１５～５０℃、最も普通には２０～４０℃であってよい。接触は、いかなる慣用的手段、例えば浸漬、吹付けまたは水平浸漬塗装によってもよい。

【００５１】最も適切なpHは、ある程度までは、用いられる特定の変色防止剤に、しかし主には、変色防止剤を含有するめっき浴中に存在する金属イオンに依存する。別個の段階で、めっきされた金属表面に変色防止剤を接触させる場合、pHは、変色防止剤に対して適切であり、それがめっきを侵さないよう選ばなければならない。溶液が銀めっき組成物である場合、好都合なpHは３～１０の範囲内である。溶液がビスマスめっき浴である場合、pHは１またはそれ以下であってよい。

【００５２】変色防止剤を含む溶液は、板の乾燥の前に板に適用される最終洗浄液であってよい。板は、変色防止剤を含む組成物との接触後に、その後の処理段階に付してよい。しかし、一般的には、変色防止剤を含む溶液との接触および乾燥後は、処理段階は、第一の裸板製造段階の終点に存在し、直ちに第二の部品取付け段階を実施できる。場合により、例えば、乾燥の前に脱イオン水による洗浄段階が存在してもよい。

【００５３】変色防止剤を含む溶液中の変色防止剤の濃度は、一般に、0.0001～５重量％、すなわち０．００１～５０ｇ／リットルであろう。好ましくは、変色防止剤の量は、０．００５～３重量％、最も好ましくは０．０１～２重量％、または１重量％未満でさえあると思われる。

【００５４】本発明の第二の態様の方法は、驚異的にも、金、白金またはルテニウムのような貴金属に対しても用いてよく、その場合、はんだ付け適性を向上させるであろう。

【００５５】本発明の第二の態様では、金属めっき段階は、好ましくは、浸漬／置換めっきまたは無電解めっき段階である。それは、単一のめっき組成物を用いる単一の段階からなる。最も好ましくは、めっき段階は、パッドおよび／または通し穴の金属を浸漬めっき組成物に接触させることを含む浸漬／置換めっき段階であろう。

【００５６】めっきが、好適な浸漬／置換法以外による場合、例えば無電解めっきによるならば、めっき組成物は、代替的なめっき用金属イオン、例えばニッケルを含んでもよい。

【００５７】本発明における変色防止剤の使用は、４０℃および９３％の相対湿度で９６時間、または１５０℃で２時間貯蔵したときでさえ、良好な耐変色性（湿度および酸化に対する耐性）を有する金属皮膜を与えることが判明した。光沢食刻段階を用いて平滑な表面を与えることによって、浸漬塗装に固有の多孔性が低下する結果、リフローはんだ付け工程の際に到達する高温においてさえ、耐変色特性がかなり改良される。銀イオンの移行に起因する、例えばドイツ国特許願第4,316,679 号明細書に記載されたような、銀めっきの使用に対する懸念は克服されるが、それは、本発明は、水分に対する障壁を与えることによって、銀の移行を実質的に防止することが判明したからである。

【００５８】本発明の上記の二つの態様において、浸漬めっき組成物は、より電気的陽性度が高い金属のイオンに対する錯化剤を含有するのが好ましい。

【００５９】本発明のもう一つの態様においては、より電気的陽性度が高い金属のイオン、そのようなイオンに対する錯化剤、及びより電気的陽性度が高い金属のための変色防止剤を含有する水性めっき組成物に接触させる結果、より電気的陽性度が高い金属の皮膜を形成することによって、相対的に電気的陽性度が低い金属を相対的に電気的陽性度が高い金属でめっきする、置換金属めっき法が提供される。

【００６０】本発明のこの態様においては、置換めっきができる金属のイオン、好ましくは該金属イオンに比して等モル量より多い量で存在する、該イオンに対する錯化剤を含有し、該金属のための変色防止剤を含有し、そして該イオンを該金属へと還元できる還元剤を実質的に含まない、新規めっき組成物も提供される。

【００６１】本発明のこの態様は、銀またはビスマスによるめっきに特に役立つことが見出された。したがって、記載されためっき組成物は、銀またはビスマスのイオンを含有するのが好ましい。

【００６２】本発明のこの態様に用いられるめっき組成物は、ＰＣＢ産業に用いられるいかなるめっき組成物にも基づく浸漬めっき組成物であってよい。

【００６３】本発明のこの実施態様では、好ましくは、めっき段階で金属表面をめっき組成物に接触させる前に、金属表面を浄化する。浄化は、酸性の浄化組成物、例えば当技術に公知のいかなる浄化組成物を用いることであってもよい。例は、AlphaMetals Limitedが供給する銅の調整剤であるＰＣ１１４４である。

【００６４】酸性浄化液を用いる浄化段階が存在する場合、一般に、金属表面をめっき液に接触させる前に、洗浄段階が存在することになる。

【００６５】好ましくは、いかなる浄化前の段階も光沢食刻段階を含むことになる。

【００６６】めっき組成物が錯化剤を含む場合、好まし

くは、０．１～２５０ｇ／リットル、好ましくは２～２００ｇ／リットル、最も好ましくは１０～１００ｇ／リットル、特に５０ｇ／リットル前後の量で存在する。錯化剤は、組成物の水性およびpHの条件下で水に不溶性の沈澱を形成しない、めっきする金属イオンに対するいかなる錯化剤であってもよい。錯化剤の混合物を用いてもよい。二座またはより高い座数の配位子である錯化剤を用いるのが望ましく、それは、そのような錯体の安定度定数は単座配位子より高いからである。

【００６７】適切な錯化剤の例としては、酸素含有配位子、例えば、好ましくは２個以上１０個以下の炭素原子を有するアミノ酸およびそれらの塩、ポリカルボン酸、普通はアミノ酢酸、例えばニトリロ三酢酸、または、普通は、エチレンジアミン四酢酸（ＥＤＴＡ）、ジエチレントリアミン五酢酸、Ｎ－ヒドロキシエチルエチレンジアミン三酢酸、１，３－ジアミノ－２－プロパノール－Ｎ，Ｎ，Ｎ’，Ｎ’－四酢酸、ビスヒドロキシフェニルエチレンジアミン二酢酸、ジアミノシクロヘキサン四酢酸もしくはエチレングリコール－ビス－［（β－アミノエチルエーテル）－Ｎ，Ｎ’－四酢酸］を包含するアルキレンポリアミンポリ酢酸、ならびにＮ，Ｎ，Ｎ’，Ｎ’－テトラキス－（２－ヒドロキシプロピル）エチレンジアミン、クエン酸塩および／または酒石酸塩、Ｎ，Ｎ－ジー（ヒドロキシエチル）グリシン、グルコン酸塩、乳酸塩、クエン酸塩、酒石酸塩、クラウンエーテルおよび／またはクリプタンドがある。

【００６８】銀に対して特に好適な錯化剤は、ＥＤＴＡ、ＤＴＰＡ、およびＮ，Ｎ，Ｎ’，Ｎ’－テトラキス－（２－ヒドロキシプロピル）エチレンジアミンである。錯化剤は、めっき液のpHの条件下で、めっき用金属イオンとの、水溶液に可溶性の錯体を形成しなければならない。

【００６９】ビスマスに適した錯化剤は塩化物であり、一般に、ビスマスに対する多座（すなわち二座またはより高い座数の）配位子の錯化剤を用いることは不要である。

【００７０】錯化剤は、すべてのめっき用金属イオンが錯化されるよう、化学量論的等価量または化学量論的過剰量のいずれかで用いるのが好ましい。化学量論的とは、等モル数を意味するものとする。好ましくは、錯化剤は銀イオンより高いモル濃度で存在し、モル比は、好ましくは（少なくとも１．２）：１、より好ましくは（少なくとも２．０）：１、更に好ましくは（少なくとも３）：１である。

【００７１】本発明のすべての面で用いるのに適した変色防止剤としては、例えば下記のものがある：

【００７２】（ａ）好ましくは６個以上の炭素原子、最も好ましくは１０個以上の炭素原子、一般的には３０個以下の炭素原子を有する脂肪酸アミンであって、第一級、第二級、第三級、ジアミン、アミン塩、アミド、エトキシ化アミン、エトキシ化ジアミン、第四級アンモニウム塩、第四級二アンモニウム塩、エトキシ化第四級アンモニウム塩、エトキシ化アミドおよびアミン酸化物であってよい。第一級、第二級および第三級アミン形式の腐食防止剤の例は、ＡＲＭＥＥＮtm（tmは商標を表す）である。それに続くアミン形式の腐食防止剤の例は、それぞれ、ＤＵＯＭＥＥＮtm、ＡＲＭＡＣtm／ＤＵＯＭＡＣ、ＡＲＭＩＤtm、ＥＴＨＯＭＥＥＮtm、ＥＴＨＯＤＵＯＭＥＥＮtm、ＡＲＱＵＡＤtm、ＤＵＯＱＵＡＤtm、ＥＴＨＯＱＵＡＤtm、ＥＴＨＯＭＩＤtm、ＡＲＯＭＯＸtmであって、すべてAkzo Chemie 社によって供給される。

【００７３】（ｂ）プリンおよび置換プリン。

【００７４】（ｃ）サルコシンのＮ－アシル誘導体、例えばCiba-Geigy社が供給するＳＡＲＫＯＳＹＬという範囲の製品。

【００７５】（ｄ）Ciba-Geigy社が供給するReocor 190のような有機ポリカルボン酸。

【００７６】（ｅ）置換基が、例えばヒドロキシC_1～C_4アルキルアミノ基、またはカルボニルを含有する基である置換イミダゾリン。例としては、特に（ｃ）の範疇のＮ－アシルサルコシンと組み合わせた、Ciba-Geigy社が製造するＡＭＩＮＥ　Ｏがある。

【００７７】（ｆ）アルキル基が２２個以下の炭素原子、好ましくは１１個以下の炭素原子を有し、アルキルまたはベンジル基が、場合により置換されている、アルキルもしくはアルキルベンジルイミダゾール、例えばウンデシルイミダゾール。

【００７８】（ｇ）アルキル基が２２個以下の炭素原子、好ましくは１０個以下の炭素原子を有し、アルキルまたはベンジル基が、場合により置換されている、ベンゾイミダゾール、特にアルキルアリールベンゾイミダゾール、例えば、特に好適である２－（ｐ－クロロベンジル）ベンゾイミダゾール。

【００７９】（ｈ）Witco 社が供給するＥＭＣＯＬ　ＰＳ－４１３のようなリン酸エステル。

【００８０】（ｉ）Ciba-Geigy社が供給するＲＥＯＭＥＴ　４２のような、場合により置換されたトリアゾール誘導体。例は、ベンゾトリアゾール、トリルトリアゾール、およびアルキル基の炭素原子数が１～２２、好ましくは１～１０であるアルキル置換トリアゾール誘導体である。

【００８１】（ｊ）置換テトラゾール、例えば５（３（トリフルオロメチルフェニル））テトラゾールも好適な例である。

【００８２】変色防止剤の選択は、めっきされる金属表面の金属にある程度まで依存すると思われるが、これは、当業者には明白であろう。例えば、変色防止剤を金のめっき浴に組み込もうとするならば、変色防止剤は塩化物の塩であってよいが、対照的に、銀のめっき浴を用いると、塩化物の塩は、不溶性の塩化銀の沈澱の形成を

招くことになるため、用いてはならない。

【００８３】変色防止剤は、溶液が水溶液となるよう、水溶性であるのが好ましい。しかしながら、水と混和しない変色防止剤を用いてもよいが、溶液に界面活性剤／助溶媒を含ませるのが必要なこともある。

【００８４】本発明は製造された裸板での変色を防ぎ、湿気に対する耐性を付与するのに少なからぬ利点を与える結果、裸板製造段階と部品取付け段階との間に更なる保護を与えることが判明した。はんだ付け適性は、増強されることが見出される。

【００８５】銀めっき組成物に適したpHは、２～１２であってよいが、好ましくは４～１０である。したがって、組成物はpH７までの酸性であってよい。あるいは又、組成物はアルカリ性であってもよく、７より大きいか、または７．５よりさえ大きいpHを有してよい。ビスマスのめっき液は、通常、１またはそれ以下の低いpHを有する。

【００８６】めっき組成物に緩衝剤を含ませて、組成物のpHが所望の範囲内にあることを確保してよい。緩衝剤としては、適合できるいかなる酸または塩基を含ませてもよい。適合できる酸または塩基とは、組成物に必要とされる量では銀イオンおよび／もしくは錯化剤の溶液から沈澱を生じない、酸または塩基である。例えば、塩化水素は、不溶性の塩化銀の沈澱を形成するため、銀めっき組成物には不適当である。適切な例としては、ナトリウムもしくはカリウムの水酸化物または炭酸塩があり、あるいは、酸が必要な場合、適切な酸として、クエン酸、硝酸または酢酸があってよい。ホウ酸塩、フタル酸塩、酢酸塩、リン酸塩を用いてもよいが、緩衝剤が金属塩の沈澱を生じてはならず、めっき率を抑えないことが好ましい。適切な緩衝剤は、所望の作業pHに依存するであろう。

【００８７】めっき組成物は、皮膜の均一性を改良するために、界面活性剤または湿潤剤のような任意の成分を含んでよい。界面活性剤を含ませる場合、めっき浴中で０．０２～１００ｇ／リットルの濃度で存在するような量で、組成物に導入するのが好ましい。好ましくは、０．１～２５ｇ／リットルの濃度、最も好ましくは１～１５ｇ／リットルの濃度で組み込むことになる。めっき浴に役立つ標準的ないかなる界面活性剤または湿潤剤を用いてもよい。非イオン界面活性剤が好適である。特に好適な界面活性剤は、それぞれ*Synperonic ＮＰ９（ＩＣＩ社より）、*Synperonic Ａ１４（ＩＣＩ社より）および*Ethylan ＨＢ４（Harcros 社より）のようなアルキルフェノールエトキシラート、アルコールエトキシラートおよびフェノールエトキシラートである（＊は商品名を示す）。

【００８８】本発明のめっき浴に含ませられるもう一つの任意の成分は、細粒化剤である。細粒化剤は、より高密度に充填された構造を有するめっきされる金属の、より小さい結晶を形成させることによって、めっきされた金属表面の外観を改良する。細粒化剤の適切な例としては、低級アルコール、例えば、１～６個の炭素原子を有する低級アルコール（例えば、イソプロパノール）およびポリエチレングリコール、例えばＰＥＧ　１４５０（Carbowax* 、Union Carbide 社）がある。細粒化剤は、０．０２～２００ｇ／リットルの量で組成物に組み込んでよい。より好ましくは、細粒化剤を含ませるならば、０．０５～１００ｇ／リットル、最も好ましくは０．１～１０ｇ／リットルの濃度においてであろう。いかなる非水性溶媒も、組成物の５０重量％未満、好ましくは３０重量％未満、またはめっき組成物の１０もしくは５重量％未満でさえもの量で存在しなければならない。

【００８９】特に吹付け塗布のための脱泡剤（例えばDow 社が供給するＡ１００）、染料等のような、その他の不活性の不干渉性成分を含ませてもよい。

【００９０】組成物の残余は水である。干渉性のイオンを除去した脱イオン水または他の純水を、本発明の方法に用いられるめっき組成物に用いる。

【００９１】本発明の方法に用いるめっき組成物を形成するには、好ましくは、場合によりその他の任意の成分とともに、脱イオン水、上記に定義したとおりの錯化剤、およびいかなる緩衝剤をも含む溶液を最初に調製し、より電気的陽性度が高い金属の塩を、水溶液として、予備混合したものへと形成しておいたその他の成分に加える。これは、溶液を調製する最も好都合な方法であることが判明しているが、それは、金属の塩をめっき組成物へと直接溶解しようとすることは、比較的時間がかかり、金属が銀である場合は、溶液からの銀イオンの暗い沈澱としての沈澱を招く光反応をより生じ易い傾向があるからである。

【００９２】銀塩を加えようとする組成物のpHは、pH３～１０が好ましく、最も好ましくは４～８であろう。

【００９３】成分は、それらが実質的に溶解してしまうまで混合する。銀の溶解のための熱の使用は、やはり、暗い銀の沈澱を形成させる傾向があり得ることから、不都合である。

【００９４】変色防止剤を含む溶液と裸板との接触後は、板を乾燥する。好ましくは、溶液と板との接触と乾燥の間に、洗浄後段階を存在させないことになる。

【００９５】乾燥は、いかなる手段によってもよいが、一般的には、温風を用いることであり、例えば、処理された金属を乾燥用オーブンを通過させてよい。

【００９６】本発明の方法を用いて得られた皮膜は、慣用のＨＡＬ法で得られたものより著しく均質かつ平坦である表面を形成し、有機質の保護と比較すると、皮膜は、はんだ付け操作に対してより耐性がある。更に、本発明の方法は、ニッケル／金の方法の利用より低廉かつ簡単である。

【００９７】その後の部品取付け段階では、裸板のめっきされたパッドおよび／または通し穴に部品をはんだ付けする。パッドおよび／または通し穴の金属（一般的には銅）とめっきする金属（通常、銀である）、ならびに／またはめっきする金属とはんだとは、混合し合う傾向があってよい。部品との形成された結合は、良好な電気伝導度および良好な結合強さを有する。

【００９８】部品取付けの後は、本発明のめっきされた層を覆って部品が取り付けられた仕上げられた板は、ニッケル／金の段階を用いて形成された板がそうであるような、結合の信頼性という問題に悩まされることがない。

【００９９】

【実施例】

実施例１

【０１００】ＥＤＴＡ５０ｇおよび固体水酸化ナトリウム２０．４ｇを、それらを溶解するのに充分な水と混合した組成物を調製した。続いて、脱イオン水中に硝酸銀１ｇを含む溶液を、ＥＤＴＡおよび水酸化ナトリウム溶液を含む予備混合物に加え、脱イオン水を加えて１リットルにした。様々な表面取付け特徴物、および様々な直径のめっきされた通し穴を有する銅の両面回路板を、下記の手順を用いて、銀溶液で塗装した。

【０１０１】２０容量％のH_2O_2（３５％）、０．５容量％のH_2SO_4（９６％）、２．５％の１，４－ブタンジオールの水溶液中で１分間、板に化学的に光沢を与えた。次いで、水道水による洗浄を用い、その後、１０％H_2SO_4中で１分間、酸洗いを実施した。板にもう一度水洗を施し、次いで、４０℃で４分間、銀めっき液に浸漬した。浴から取り出した後、板を水洗し、温風乾燥した。板の銅の部域は、光沢のある平坦な銀析出物で塗装された。

【０１０２】被覆した板を、代表的なＩＲはんだペーストのリフロー特性像を通過させる３回のパスに付し（リフローパスについての時間に対する温度の適切な例を示す図１を参照されたい）、次いで、ＮＲ３００というAlpha Metals Limitedの、ＶＯＣ（揮発性有機化合物）を含まないノークリーン融剤を用いて、ウェーブはんだ付けを実施した。めっきされた通し穴の、はんだによる１００％の充填が達成された。

【０１０３】更に、板を湿潤キャビネット内に４０℃／９３％のRH（相対湿度）で２４時間貯蔵してから、３回のＩＲリフロー特性像を通過させた。これらの板は、銀皮膜上に軽度の変色を示した。しかし、ＮＲ３００の融剤によるその後のウェーブはんだ付けの間に、穴の１００％の充填がやはり達成された。

【０１０４】実施例２

【０１０５】脱イオン水８００ml中にＥＤＴＡ５０ｇ、ＮａＯＨ２０．４ｇ、Ethylan HB４（Akros Chemicals 社）１４ｇ、Crodamet０２（Croda Chemicals 社）３ｇを含む溶液を形成することによって、銀めっき液を調製した。この溶液に、脱イオン水１００ml中の$AgNO_3$ １ｇの溶液を加えた。希ＮａＯＨ／HNO_3の添加によって、pHを６．８に調整し、次いで、脱イオン水を用いて１リットルにした。

【０１０６】実施例１に記載の手順を用いて、銅の両面裸板を上記溶液で塗装した。３回のＩＲリフロー特性像を通過させた後、ＮＲ３００の融剤によるウェーブはんだ付けの際に、めっきされた通し穴の、はんだでの１００％の充填が達成された。

【０１０７】３回のＩＲリフロー特性像を通過させる前に、４０℃／９３％のRHで２４時間貯蔵した板は、変色の証拠を全く示さず、ウェーブはんだ付け試験の際に充分にはんだ付けされ、穴の１００％の充填がなされた。

【０１０８】実施例３

【０１０９】実施例１に記載の浴組成物および手順を用いて、銅の両面裸板を塗装した。銀めっき液から板を取り出し、洗浄した後に、Reomet４２（Ciba-Geigy社）４ｇの脱イオン水１リットル中の溶液（pH７）に室温で１分間浸漬した。次いで、板を水道水で洗浄し、温風乾燥した。光沢のある平坦な銀皮膜が形成された。

【０１１０】塗装した板を４０℃／９３％のRHで２４時間貯蔵し、次いで、３回のＩＲペーストのリフロー特性像を通過させた。板は、変色の証拠を全く示さず、ＮＲ３００の融剤を用いてウェーブはんだ付けしたときに、充分にはんだ付けされた。

【０１１１】実施例４

【０１１２】実施例２に記載のとおり、短冊状の銅クーポン（５cm×１cm）を銀皮膜で塗装した。加えて、浸漬スズ塗装、６３／３７のＳｎ／Ｐｂによる塗装、および置換ベンゾイミダゾールの化学に基づく２種類の錯合物質によるはんだ付け適性保存塗装を用いて、更にいくつかの試料を塗装した。様々な試料に対して、下記の塗装手順を適用した：

【０１１３】浸漬スズ塗装

【０１１４】クーポンを、$Na_2S_2O_8$（５％）、H_2SO_4（５％）の水溶液中で２分間食刻し、水道水で洗浄し、次いで１０％のH_2SO_4で１分間洗浄し、次いで脱イオン水で洗浄した。次いで、クーポンを、脱イオン水中に３３ｇ／リットルの$Sn(BF_4)_2$、１５０ｇ／リットルのチオ尿素、２０ｇ／リットルのフルオロホウ酸および５ｇ／リットルのSynperonic　ＮＰ９（ＩＣＩ社より）を含む浸漬スズめっき液に室温で１分間浸漬した。次いで、クーポンを脱イオン水で洗浄し、温風乾燥した。

【０１１５】Ｓｎ／Ｐｂ塗装

【０１１６】クーポンを、$Na_2S_2O_8$（５％）、H_2SO_4（５％）を含む水溶液中で食刻し、水道水、次いで１０％のH_2SO_4、次いで脱イオン水で洗浄した。クーポンを温風乾燥した。次いで、Alpha 社のＮＲ

３００という融剤を各クーポンに塗布した。次いで、溶融はんだへの２５０℃で3秒間の浸漬によって、クーポンを６３／３７のＳｎ／Ｐｂで塗装した。

【０１１７】アゾール１およびアゾール２

【０１１８】浸漬スズの試料についてのとおりに、クーポンを食刻かつ洗浄した。次いで、アゾールを含有する溶液に４０℃で９０秒間、クーポンを浸漬した。アゾール含有溶液から取り出した後、クーポンを脱イオン水で洗浄し、温風乾燥した。

【０１１９】クーポンを各種の異なる前処理に付した。

【０１２０】Ａ．前処理は全くなし。

【０１２１】Ｂ．３回のはんだペーストによるリフロー特性像を通過。

【０１２２】Ｃ．４０℃／９３％のRH（相対湿度）で９６時間貯蔵。

【０１２３】Ｄ．４０℃／９４％のRHで９６時間貯蔵し、次いで、３回のはんだペーストによるリフロー特性像。

【０１２４】Ｅ．１５０℃で2時間貯蔵。

【０１２５】次いで、ＮＲ３００融剤によるメニスコグラフを用いて、試料をはんだ付けした。

【０１２６】メニスコグラフ試験法は、標本とはんだとの間に作用する正味の力を測定することによって、はんだ適性を監視する。皮膜は、平衡湿潤力に達する時間の長さ、および平衡湿潤力の大きさを測定することによって評価される。ウェーブはんだ付けで良好な結果を達成するには、短時間の湿潤、および高い平衡湿潤力が好ましい。

【０１２７】下記の表は、銅で被覆した様々な試料についての湿潤時間を秒で、および浸漬の２秒後の湿潤力をmN/mmで示す。

【０１２８】

【表１】

皮　膜	前　処　理	湿潤時間／秒	湿潤力／２秒
実施例２	A	0.7	0. 29
実施例２	B	0.8	0.444
実施例２	C	0.7	0.429
実施例２	D	0.7	0.441
実施例２	E	0.8	0.438
ス　ズ	A	0.9	0.488
ス　ズ	B	>5	−0.028
ス　ズ	C	>5	0.008
ス　ズ	D	>5	−0.148
アゾール１	A	0.8	0.439
アゾール１	B	0.9	0.412
アゾール１	C	0.9	0.443
アゾール１	D	0.8	0.426
アゾール１	E	1.0	0.421
アゾール２	A	0.8	0.449
アゾール２	B	1.0	0.417
アゾール２	C	0.9	0.466
アゾール２	D	1.1	0.310
アゾール２	E	1.2	0.296
Ｓｎ／Ｐｂ	A	0.8	0.475
Ｓｎ／Ｐｂ	B	0.8	0.501
Ｓｎ／Ｐｂ	C	0.8	0.492
Ｓｎ／Ｐｂ	D	0.8	0.474
Ｓｎ／Ｐｂ	E	0.8	0.492

【０１２９】上記から理解できるとおり、本発明に従って調製した銀皮膜は、Ｓｎおよびベンゾイミダゾールという代替策より短い湿潤時間および高い湿潤力を有し、湿度および熱の処理後は、これらの特性をより容易に保持する。

【０１３０】実施例５

【0131】酸化ビスマス3．9g、塩化水素183．1g（37%溶液として）、グリコール酸490．5g（70%溶液）、265．4g（50%水酸化ナトリウム溶液）、ヨウ化カリウム0．077g、Synperonic NP9（ICI社より）0．003gおよび2p－クロロベンジルベンゾイミダゾール4gを含む置換ビスマスめっき組成物を調製し、脱イオン水に加えて、製品溶液1リットルを作製した。銅のパッドおよび銅の通し穴を有する裸板に、実施例1に記載のとおり、化学的に光沢を与え、次いで、70℃で2分間めっき浴に浸漬した。銅の表面に、0．05μm の肉厚を有するビスマスの皮膜が形成された。めっきされた裸板に対して実施したその後のはんだ付け適性および耐変色性の試験は、はんだ付け適性および耐変色性について良好な結果を示した。

【0132】実施例6

【0133】銅の両面裸板を、50容量%のHNO_3、10%のH_2SO_4、10%のH_3PO_4、1%のHC1の水溶液中で室温で1分間、光沢食刻した。次いで、板を水道水で洗浄し、その後10%のH_2SO_4で1分間洗浄した。もう一度水洗した後、実施例2に記載の銀めっき浴に45℃で4分間、板を浸漬した。次いで、板を水洗し、温風乾燥した。

【0134】塗装した板を、40℃／93%のRHで24時間貯蔵し、IRペーストによるリフロー特性像を3回通過させた。板は、変色の証拠を全く示さず、NR300融剤を用いてウェーブはんだ付けしたときに、充分にはんだ付けされた。

【0135】実施例7

【0136】ジエチレントリアミン五酢酸64．8g、NaOH23．0g、界面活性剤であるEthylan　HB4（Akros Chemicals 社）14g、Crodamet　02というエトキシ化第三級アミン化合物（Croda Chemicals 社）2．5gを脱イオン水800ml中に含む溶液を形成することによって、銀めっき浴を調製した。この溶液に、脱イオン水100ml中の硝酸銀1gの溶液を加えた。希NaOH溶液または硝酸の添加によって、この溶液のpHを6．9に調整した。次いで、脱イオン水を用いて、容量を1リットルにした。

【0137】実施例1に記載の手順を用い、上記溶液を用いて、銅の両面裸板を塗装した。3回のIRリフロー特性像を通過させた後、Alpha Metals社のNR300融剤を用いた塗装した板のウェーブはんだ付けの際に、めっきされた通し穴の100%の充填が達成され、変色の証拠を全く示さず、ウェーブ試験の際に充分にはんだ付けされて、穴の100%の充填が行われた。

【0138】実施例8

【0139】脱イオン水98．2g、硝酸1g、硝酸銀0．1g、Chemeen　C2（変色防止剤）0．3gおよびMazawet　DF（可溶化剤）0．4gを含む浸漬銀めっき液を調製した。エチレンジアミンの50%溶液を用いて、pHを6に調整した。この浴は、接着性の銀析出物を銅のクーポン上に形成し、良好なはんだ付け適性および耐湿性を示した。

【0140】実施例9

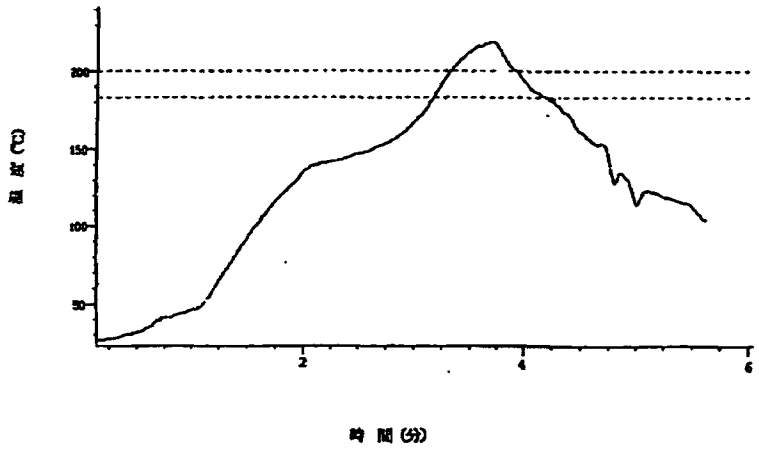
【0141】2．1重量%の三酸化ビスマス、46．73重量%の塩酸（22ボーメ度）、49．5重量%のグリコール酸（70%）、0．07重量%の塩化カリウム、0．1重量%のポリエチレングリコール600、0．2重量%のChemax ChemeenC2、1．2重量%の蒸留水および0．1重量%の酒石酸を含有するビスマスめっき液を調製した。Chemeen C2を除去したもう一つの溶液を調製した。銅被覆プリント回路材料の試料を各溶液中でめっきした。次いで、これらのめっきされた試料を60℃、95%相対湿度の湿潤室に16時間置いた。

【0142】この曝露の後、試料を検査し、Chemeen C2を含まない溶液中で調製したものは、激しく変色していた。変色防止剤を含有する溶液中で調製した試料は、最小限の酸化による良好な外見を有し、試験したときに、良好なはんだ付け可能性を示した。

【図面の簡単な説明】

【図1】図1は、リフローパスについての時間に対する温度の適切な例を示す。

【図1】



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【外国語明細書】

1. Title of Invention

PRINTED CIRCUIT BOARD MANUFACTURE

2. Claims

1. A method for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising contacting the pads and/or through-holes with a bright etch composition in a bright-etch step; and subsequently metal plating the etched pads and/or through-holes by contact with a plating composition comprising ions of a metal which is more electropositive than the metal from which the pads and/or through-holes are formed and being substantially free of reducing agent for said ions in an immersion metal plating step to form solderable plated metal surfaces.

2. A method according to claim 1 in which the plated metal surfaces are contacted with a solution of a tarnish inhibitor.

3. A method for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of tarnish inhibitor.

4. A method according to claim 3 in which the metal plating step is a method in which a metal which is more electropositive than the metal of the said pads and/or through-holes is immersion/displacement coated from an aqueous solution containing ions of the more electropositive metal and being substantially free of reducing agent for said ions.

5. A method according to any preceding claim in which the plating composition contains a complexing agent for the said ions, preferably a multidentate ligand complexing agent.

6. A method according to any of claims 2 to 4 in which the plating composition comprises a tarnish inhibitor and in the process, the metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step so that the tarnish inhibitor is present in the metal plating composition.

7. A method according to any of claims 2 to 4 in which the metal plated surfaces are formed in the plating step and subsequently the pre-formed plated metal surfaces are contacted with a solution comprising a tarnish inhibitor in a post-rinse second step.

8. A method according to any of claims 2 to 4, 6 or 7 in which the contact time of the plated metal surfaces with the solution comprising a tarnish inhibitor is from 10 seconds to 5 minutes.

9. A method according to any of claims 2 to 4 and 6 to 8 in which the metal surfaces are contacted with a solution comprising a tarnish inhibitor by dip coating or spray coating.

10. A method according to any of claims 2 to 4 and 6 to 9 in which the tarnish inhibitor is present in the solution in an amount of from 0.001 to 5% by weight of the solution.

11. A method according to any preceding claim in which the metal coating of the plated metal surfaces comprise nickel, silver, tin, lead, palladium, cobalt, gold, platinum or bismuth or their alloys, preferably silver.

12. A method according to any preceding claim in which the pads or through holes are formed of copper.

13. A method according to any preceding claim including a preliminary step of applying to exposed conductor traces at the surface of the PCB a mask which is an insulator, such that the pads and/or through-holes are left exposed.

14. A method according to any preceding claim including a subsequent step of attaching conducting components to the metal plated pads and/or through-holes using solder in direct contact with the metal plating.

15. An aqueous plating composition suitable for forming an immersion plating of a relatively more electropositive metal on a relatively less electropositive metal substrate containing ions of the more electropositive metal and a complexing agent for the ions and a tarnish inhibitor for the more electropositive metal and being substantially free of reducing agent for said ions.

16. A composition according to claim 15 in which the tarnish inhibitor is present in the solution in an amount of from 0.001 to 5% by weight of the composition.

17. A composition according to claim 15 or 16 in which the said ions are of nickel, silver, tin, lead, palladium, cobalt, gold, platinum or bismuth or their alloys, preferably silver.

3. Detailed Description of Invention

In the production of a printed circuit board (PCB), in a first (multi-step) stage a "bare board" is prepared and in a second (multi-step) stage, various components are mounted on the board. The present invention relates to the final steps in the manufacture of the bare board, in which the bare board is coated with a protective layer prior to passing to the second production stage.

There are currently two types of components for attachment to the bare boards in the second stage: legged components eg resistors, transistors etc and, more recently, surface mount devices. Legged components are attached to the board by passing each of the legs through a hole in the board and subsequently ensuring that the hole around the leg is filled with solder. Surface mount devices are attached to the surface of the board by soldering with a flat contact area or by adhesion using an adhesive.

In the first stage, a board comprising an insulating layer, a conducting circuit pattern and conductive pads and/or through-holes is produced. The board may be a multi-layer board having more than one conducting circuit pattern positioned between insulating layers or may comprise one insulating layer and one conducting circuit pattern.

The through-holes may be plated through so that they are electrically conducting and the pads which form the areas to which the surface-mount components will be attached in the subsequent component-attachment stage, are also electrically conducting.

The conductive areas of the circuit pattern, pads and through-holes may be formed from any conductive material or mixtures of different conductive materials. They are generally however, formed from copper. Since over time, copper tends to oxidise to form a copper oxide layer with

poor solderability, prior to passing to the second, component-attachment stage, a protective layer is coated over the pads and/or through-hole areas where it is desired to retain solderability to prevent formation of a poorly solderable surface layer of copper oxide.

Whilst there is more than one way for preparing the bare boards, one of the most widely used processes for making the bare boards is known as the "solder mask over bare copper" (SMOBC) technique. Such a board generally comprises an epoxy-bonded fibreglass layer clad on one or both sides with conductive material. Generally, the board will be a multi-layer board having alternate conductive layers which comprise circuit pattern, and insulating layers. The conductive material is generally metal foil and most usually copper foil. In the SMOBC technique, such a board is obtained and holes are drilled into the board material using a template or automated drilling machine. The holes are then "plated through" using an electroless copper plating process which deposits a copper layer on the entirety of the board: both on the upper foil surfaces and on the through-hole surfaces.

The board material is then coated with a light sensitive film (photo-resist), exposed to light in pre-selected areas and chemically developed to remove the unexposed areas revealing the conductive areas which are the plated through-holes and pads. Generally, in the next step, the thickness of the metal foil in the exposed areas is built up by a further copper electroplating step. A protective layer of an etch resist, which is usually a tin-lead alloy electroplate composition is applied over the exposed and thickened copper areas.

The photo-resist is then removed exposing the copper for removal and the exposed copper surface is etched away using a copper etching composition to leave the copper in the circuit pattern finally required.

In the next step, the tin-lead alloy resist is stripped away.

Since components will not be attached to the copper circuit traces, it is generally only necessary to coat the solder for attaching the components over the through-hole and pad areas but not the traces. Solder mask is therefore applied to the board to protect the areas where the solder coating is not required, for example using a screen printing process or photo-imaging technique followed by development and, optionally curing. The exposed copper at the holes and pads is then cleaned and prepared for solder coating and the protective solder-coating subsequently applied, for example by immersion in a solder bath, followed by hot air levelling (HAL) to form a protective solder coating on the areas of copper not coated with solder mask. The solder does not wet the solder mask so that no coating is formed on top of the solder-mask protected areas.

At this stage, the board comprises at least one insulating layer and at least one conductive layer. The conductive layer or layers comprise a circuit trace. The board also comprises a pad or pads and/or through-hole(s) protected from tarnishing by layer of solder. A single conductive layer may comprise either a circuit trace or pad(s), or both. Any pads will be part of a conductive layer which is an outerlayer of a multi-layer board. The circuit traces on the board are coated with solder mask.

Such a board is ready to proceed to the second stage for attachment of the components. In this second stage, generally attachment of the components is achieved using solder: firstly a layer of solder paste (comprising solder and flux) is applied onto the boards, generally by printing and the components are positioned on the printed boards. The board is then heated in an oven to produce fusion of the solder in the solder paste, which forms a contact between the components and the board. This process is known as reflow soldering. Alternatively a wave soldering process is used in which the board is passed over a bath of

molten solder. In either case additional solder is used over and above any protective solder coating.

The additional complications of attaching both legged components and the surface mount devices and the special requirements for mounting many small closely spaced components have resulted in increased demands on the surface protection coating for the conductive metal to which the components will be attached, on the PCB's. It is essential that the finish applied by the bare board manufacturer does not leave a pad with an uneven surface as this increases the risk of electrical failure. It is also essential that the protective coating does not interfere in the subsequent solder step, thereby preventing formation of a ' good, conducting bond between the bare board and components. An extra step in which the protective coating is removed would be undesirable.

As explained above, the conductive metal surfaces are generally formed of copper and the protective surface must be applied at the end of the first stage to prevent the formation of non-solderable copper oxide on the copper surfaces prior to the component attachment. This is particularly important because generally speaking, the first stage and the second, component-attachment stage will be carried out on completely different sites. There may therefore be a considerable time delay between formation of conducting pads and/or through holes and the component attachment stage, during which time oxidation may occur. Therefore, a protective coating is required which will retain the solderability of conducting material and enable a soldered joint to be made when the components are attached to the bare boards.

The most common protection coating presently used is tin/lead solder, generally applied using the "HAL" (Hot air levelling) process, an example of which is described in detail above.

HAL processes are limited because it is difficult to apply the solder evenly and the thickness distribution

produced by the use of HAL processes makes it difficult to reliably attach the very small and closely spaced components now being used.

Several replacement treatments for the HAL coating of a solder layer are being introduced. The coatings must enable formation of a reliable electrical contact with the component. They should also be able to stand up to multiple-soldering steps. For example, as described above there are now both legged and surface mount components for attachment to the bare boards and these will generally be attached in at least two soldering operations. Therefore, the protective coatings must also be able to withstand at least two soldering operations, so that the areas to be soldered in a second operation remain protected during the first operation.

Alternatives to the tin/lead alloy solder used in the HAL process which have been proposed include organic protection, immersion tin or tin/lead plating and nickel/gold plating. In the nickel/gold process electroless plating of the copper surfaces is carried out in which a primer layer of nickel is applied onto the copper followed by a layer of gold. This process is inconvenient because there are many process steps and in addition, the use of gold results in an expensive process.

Organic protection for the copper pads during storage and assembly prior to soldering have also been effected using flux lacquer. Its use is generally confined to single-sided boards (ie. boards which have conductive pads on only one side). The coating is generally applied by dip, spray or roller coating. Unfortunately, it is difficult to provide a consistent coating to the board surfaces so limited life expectancy, due to the porosity of the coating and to its inconsistent coating thickness, results. Flux lacquers have also been found to have a relatively short shelf life. A further problem is that in the component-attachment stage, if reflow soldering is to be used to attach the components, the components are held

in place on the underside of the boards with adhesive. In cases where the flux lacquer is thick, the adhesive does not bond the component directly to the printed board, but instead forms a bond between the adhesive and the lacquer coating. The strength of this bond can drop during the fluxing and soldering step causing components to be lost during contact with the solder baths.

One other alternative currently being used is passivation/protection treatment based upon the use of imidazoles or triazoles in which copper-complex compounds are formed on the copper surface. Thus, these coatings chemically bond to the surface and prevent the reaction between copper and oxygen. However this process is disadvantageous because it tends to be inadequate for withstanding successive soldering steps so that the high temperatures reached in a first soldering step tend to destroy the layer which cannot withstand a subsequent soldering operation needed to mount further components. One example of such a process is given in EP-A-0428383, where a process is described for the surface treatment of copper or copper alloys comprising immersing the surface of copper or copper alloy in an aqueous solution containing a benzimidazole compound having an alkyl group of at least 3 carbon atoms at the 2-position, and an organic acid.

Processes are also known which provide coatings using compositions which comprise silver.

The three common complexing systems for electroless silver plating processes are either ammonia- based, thiosulphate-based or cyanide-based.

The ammonia systems are disadvantageous because the ammonia-containing silver solutions are unstable and explosive azides may tend to form. Thiosulphate systems are disadvantageous for use in the electronics industry because sulphur compounds in the silver coatings formed result in poor solderability so that in the subsequent component-attachment step, a poor electrical contact may be formed between the bare board and the component.

The cyanide-based systems are disadvantageous due to the toxicity of the plating solutions.

In US-A-5318621 an electroless plating solution containing amino acids as rate enhancers for depositing silver or gold onto a nickel coating overlying copper on a circuit board is disclosed. It is described that neither gold nor silver electroless plating baths based on thiosulphate/sulphate will plate directly onto copper because the copper rapidly dissolves without allowing a silver or gold coating to form. In the introduction of this reference, "Metal Finishing Guidebook & Directory" (1993 edition) is discussed. Silver plating solutions comprising silver nitrate, ammonia and a reducing agent such as formaldehyde are mentioned.

US-A-4863765 also discloses electroless silver plating, using a cyanide-based plating solution. In Metal Finishing (1983) 81(1), pp 27-30 Russev describe immersion silvering of copper powder from a plating solution containing silver nitrate and a nitrogen complexing agent. In Metal Finishing (1960) August, p 53 Geld describes a silver coating process involving an initial bright dip of the brass or copper substrate, followed by a silver plating step in which a thick coating of silver is plated from a solution of silver nitrate and potassium iodide. The process is for plating of electrical contacts to increase conductivity.

In JP-A-04-110474 a base material is plated with silver, dried and subsequently treated with a mercaptan compound to prevent tarnish.

In DE-C-4316679 base metals such as copper are coated with palladium in a two-step process including a first-step in which the surface is contacted with a bath containing a palladium salt and an oxidising agent, and in the second step with a bath containing a palladium salt, a complexing agent and formic acid or formic acid derivative. The latter bath may also contain stabilisers for the bath itself, which stabilise the bath against decomposition or

"plating-out". It is suggested that the copper substrate should previously be etched using a non-bright atch bath including persulphate. However such pretreatment steps tend to produce relatively porous coatings. The inventors minimise the porosity of the coating by using the two-step process in the first of which a very thin coating is formed. This reference warns against using silver as corrosion protection due to migration.

The present invention relates to a displacement immersion metal-plating in which a more electropositive metal displaces a less electropositive metal at the surface to be coated. Ions of the more electropositive metal oxidise the substrate metal. A displacement plating process differs from an electroless process because the silver coating forms on the surface of a metal by a simple displacement reaction due to the relative electrode potentials of the oxidisable metal of the surface to be protected and of the silver ions respectively.

It is reported in for example "Modern Electroplating" by F.A. Lowenheim, published by J Wiley & Sons (1963) that silver will plate by displacement on most base metals but that immersion plated silver is poorly adherent. F.A. Lowenheim suggests that when electroplating base metals with silver, it is necessary to deposit first a thin film of silver on the work piece from a high-cyanide strike bath to ensure good adhesion of the subsequent electroplated silver layer.

The present invention aims to provide an alternative to the solder protection coating for the copper or other conducting surfaces of bare boards which require protection from tarnishing between bare board manufacture and the component-attachment stage.

In accordance with the present invention there is provided a method for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the process

comprising contacting the pads and/or through holes with a bright-etch composition in a bright-etch step; and subsequently immersion plating the etched pads and/or through holes in a metal-plating step to form solderable plated metal surfaces.

The insulating layer and conducting layer of the PCB will be as described above. They may comprise the insulating layer and conducting circuit pattern of any conventional PCB, respectively. The pads and/or through holes for plating are those areas of the PCB for which solderability must be maintained for attachment of components in the subsequent soldering steps for component-attachment.

The bright-etch step comprises contacting the pads and/or through-holes with a bright etch composition. Such compositions are already known in the industry for other applications and they produce a bright smooth cleaned surface on the conducting metal from which the pads and/or through-holes are formed. In contrast, non-bright etch compositions, such as those which are based on persulphate provide microroughened, cleaned surfaces. The use of the bright etch step allows the formation of a dense, non-porous metal coating, which is particularly suitable for a subsequent soldering step.

Suitable bright-etch compositions are generally aqueous and may be based for example on one or mixtures of more than one of hydrogen peroxide, sulphuric acid, nitric acid, phosphoric acid or hydrochloric acid. The bright etch compositions generally include at least one component which will tend to modify the dissolution of copper in bright-etch compositions.

Particularly preferred bright etch compositions where the metal surface of the pads and/or through-holes comprises copper or a copper alloy are, for example as described in JP 62-188785 A2 (comprising 5.1-10.2 moles/ℓ nitric acid, 4.6-9.2 moles/ℓ sulphuric acid, 0.01 moles/ℓ zinc nitrate and 0.4 moles/ℓ copper nitrate in aqueous

solution); JP 60-190582 (comprising for example 20-50% by weight sulphuric acid (96%), 10-35% by weight nitric acid (67.5%), 0.5-1% by weight hydrochloric acid (35%) and 0.5-1% by weight nonionic surfactant); US-A-3668131 (comprising hydrogen peroxide, sulphuric acid and urea additives); Metal Finishing (Feb 1986), 84, (2), 67-70 (comprising sodium dichromate, sulphuric acid, hydrochloric acid, sodium diethyldithio carbonate); Trans Inst. Metal Finishing (Summer 1983), 61, (2), 46-49 (acidified hydrogen peroxide comprising hydrogen peroxide, sulphuric acid and stabiliser); Oberfläche Surf, (Aug 1979) 20, (8), 178-179 (comprising nitric acid and dodecyl pyridinium chloride); US-A-4510018 (comprising sulphuric acid, hydrogen peroxide, fatty acid amine and ammonium compound); US-A-4459216 (comprising 5-100g/ℓ hydrogen peroxide and 100-300 g/ℓ sulphuric acid and aromatic stabiliser); JP 84-038308 (comprising 0.15-0.3 moles/ℓ hydrochloric acid; 0.2-0.4 moles/ℓ phosphoric acid and 0.02-0.1 moles/ℓ sulphuric acid). Where the conducting material of the pads and/or through-holes comprises stainless steel, particularly preferred bright-etch compositions may be as described for example in WO 93-08317; JP 62-238379 A2; DE 1928307; or Tr. Gos. Nauchno-Issled. Proektn. Inst. Osnovn. Khim (1974), 36, 93-97. Where the conducting material is aluminium, a suitable bright-etch is as described in Met. Finishing (July 1986) 84, (7), 55-59.

Thus any etch composition which provides a bright, cleaned surface may be used. In the bright-etch step, contact with the bright-etch composition may be by immersion, spray or any other coating technique, such as is described in any of the references above, for sufficient time and at a suitable temperature to enable a bright surface to form on the conducting material of the pads and/or through-holes. Generally the temperature for contact with the bright-etch composition will be ambient and the contact time will be from 5 seconds to 10 minutes,

praferably at least 30 seconds, or even at least 2 minutes, and preferably for no greater than 5 minutes.

Generally after the etching step, there will be a post-rinse step comprising rinsing with deionised water and generally without drying, the bare boards then proceed directly to the plating step. Alternatively, an acid rinse step may be included, after the aqueous rinse.

The plating step is an immersion (or displacement) plating step.

In an immersion plating step, the plating composition comprises metal ions of a metal which is more electropositive than the conducting material. The choice of metal ions in the immersion plating solution, therefore depends on the metal to be plated. Since the pads or through-holes generally comprise copper or nickel, suitable examples of plating metals include bismuth, tin, palladium, silver and gold; silver and bismuth ions are particularly preferred.

A particularly preferred immersion silver plating method is described in our copending British application filed today under the reference number 64/2031/00.

As sources of plating metal ions, any water soluble metal salt may be used, for example nitrates, acetates, sulphates, lactates or formates. Preferably silver nitrate is used.

The metal plating ions are generally in the plating composition at a concentration of from 0.06 to 32 g/l (based on metal ions), preferably from 0.1 to 25 g/l, most preferably from 0.5 to 15 g/l.

Contact of the metal surface with the plating solution will generally be at temperatures of from 10 to 90°C, preferably 15 to 75°C, more preferably 20 to 60°C. For example, the temperature of contact with the plating solution will be from 15 to 50°C, most usually from 20 to 40°C.

Contact can be by any method, usually dip, spray or horizontal immersion coating. Spray coating is preferred.

Such contact may be part of a substantially continuous coating process.

The contact time of the plating solution with the metal surface is sufficient to form plated metal surfaces over the metal. Generally the contact time will be from 10 seconds to 10 minutes. A contact time of less than 10 seconds has generally being found to give insufficient coverage with silver coating and although the contact time may be longer than 10 minutes, no additional benefit has been found from a contact time of longer than 10 minutes.

The preferred plating process is an immersion displacement process and not a true electroless plating process. In the preferred plating compositions of the present invention, metal atoms on the surface of the metal are oxidised by the metal plating ions in the solution, so that a layer of plated metal deposits on the pads and/or through holes. The process is self-limiting because when plated metal covers all of the surface sites of metal oxidisable by the plating metal no further reaction and therefore no further deposition occurs.

In a second aspect of the invention there is provided for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of a tarnish inhibitor.

In this aspect of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited. Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step

prior to contacting the metal surface with the plating solution. Preferably any pre-cleaning will include a bright-etch step.

In both aspects of the invention the tarnish inhibitor may be present in the plating solution itself so that the plating solution comprises the solution comprising tarnish inhibitor. Thus, in a preferred method of the invention, the plated metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step (i.e. contact may be during formation of the plated metal surfaces).

Alternatively, the metal surfaces are formed in the plating step and subsequently the formed metal surfaces are contacted with a solution comprising a tarnish inhibitor in a further step. The solution is preferably aqueous, being made up from deionised or otherwise purified water. The composition comprising tarnish inhibitor may additionally comprise solubilisers, for example non-aqueous solvents, surfactants and/or pH buffers.

Contact of the composition comprising tarnish inhibitor with the plated metal surfaces will be for at least 5 seconds, preferably for at least 20 seconds. Where the tarnish inhibitor is present in the plating solution, the time of contact is generally determined by the duration of the plating step. Generally, the contact time will be from 1 to 5 minutes. The temperature of contact is most usually from 10 to 90°C, preferably 15 to 75°C, more preferably 20 to 60°C. For example the temperature of contact with the plating solution may be from 15 to 50°C, most usually from 20 to 40°C. Contact may be any conventional means, for example by dip, spray or horizontal immersion coating.

The most appropriate pH depends to some extent on the particular tarnish inhibitor used but primarily on the metal ions present in a plating bath which contains the tarnish inhibitor. Where the tarnish inhibitor is contacted in a separate step with the plated metal surface,

the pH should be appropriate for the tarnish inhibitor and selected so that it does not attack the plating. Where the solution is a silver plating composition a convenient pH is in the range 3 to 10. Where the solution is a bismuth plating bath the pH may be 1 or lower.

The solution comprising the tarnish inhibitor may be a final rinse solution, applied to the boards prior to drying of the boards. The board may undergo subsequent treatment steps after contact with the composition comprising tarnish inhibitor. However, generally, after contact with the solution, comprising a tarnish inhibitor and drying, they are at the end of the first bare board manufacturing stage, and are ready for the second component-attachment stage. Optionally, for example, there may be a deionised water rinse step, prior to drying.

The concentration of tarnish inhibitor in the solution comprising tarnish inhibitor, will generally be from 0.0001 to 5% by weight, i.e. 0.001 to 50g/l. Preferably, the amount of tarnish inhibitor will be from 0.005 to 3% by weight, and most preferably from 0.01 to 2% by weight, or even below 1% by weight.

The method of the second aspect of the invention may surprisingly also be used on precious metals such as gold, platinum or ruthenium where it will improve solderability.

In the second aspect of the invention the metal plating step is preferably an immersion/displacement plating or electroless plating step. It consists of a single step using a single plating composition. Most preferably the plating step will be an immersion/displacement plating step comprising contacting the metal of the pads and/or through-holes with an immersion plating composition.

Where the plating is other than by the preferred immersion/displacement process, for example if it is by electroless plating the plating composition may comprise alternative plating metal ions, such as nickel.

The use of tarnish inhibitor in the invention has been found to provide metal coatings which have good tarnish-resistance (resistance to humidity and oxidation) even when stored at 40°C and 93% RH for 96 hours or at 150°C for 2 hours. The porosity inherent in immersion coatings is reduced by the provision of a level surface using the bright-etch step so that the anti-tarnish properties are considerably improved, even at the high temperatures reached in reflow soldering processes. Concern over the use of silver plating as described for example in DE-C-4315679 due to migration of silver ions is overcome as it has been found that the present invention substantially prevents silver migration by providing a barrier to moisture.

In both the above aspects of the invention, an immersion plating composition preferably contains a complexing agent for the ions of the more electropositive metal.

In a further aspect of the present invention there is provided a displacement metal plating process in which a relatively less electropositive base metal is plated with a relatively more electropositive coating metal by contact with an aqueous plating composition containing ions of the more electropositive metal, a complexing agent for such ions and a tarnish inhibitor for the more electropositive metal so as to form a coating of the more electropositive metal.

In this aspect of the invention there is also provided a new plating composition containing ions of a metal which can be displacement plated, a complexing agent for the ions, preferably present in higher than equimolar amounts as compared to the metal ion, and containing a tarnish inhibitor for the said metal, and being substantially free of reducing agent capable of reducing the ions to the metal.

This aspect of the invention has been found to be particularly useful for silver or bismuth plating.

Therefore preferably, the plating composition described contains silver or bismuth ions.

The plating composition used in this aspect of the invention may be a immersion plating composition based on any plating composition used in the PCB industry.

In this embodiment of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited.

Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step prior to contacting the metal surface with the plating solution.

Preferably any pre-cleaning will include a bright-etch step.

Where the plating composition comprises a complexing agent it is preferably present in an amount of from 0.1 to 250 g/l, preferably from 2 to 200 g/l and most preferably from 10 to 100 g/l, especially around 50 g/l. The complexing agent may be any complexing agent for the plating metal ions which does not form a water insoluble precipitate under the aqueous and pH conditions of the composition. Mixtures of complexing agents may also be used. It is desirable to use complexing agents which are bi-dentate or higher dentate ligands since the stability constants of such complexes are higher than mono-dentate ligands.

Examples of suitable complexing agents have oxygen-containing ligands, for instance amino acids and their salts, preferably having at least 2 and up to 10 carbon atoms, polycarboxylic acids, usually amino acetic acids, such as nitrilo-triacetic acid or, usually, alkylene polyamine polyacetic acids including ethylene diamine tetracetic acid (EDTA) diethylene triamine pentaacetic

acid, N-hydroxyethyl ethylene diamine triacetic acid, 1,3-diamino-2-propanol-N,N,N,'N,'-tetra-acetic acid, bishydroxyphenylethylene diamine diacetic acid, diamino cyclohexane tetraacetic acid or ethylene glycol-bis-[(β-aminoethylether)-N,N'-tetraacetic acid] and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine, citrates and/or tartrates, N,N-di-(hydroxyethyl)glycine, gluconates, lactates, citrates, tartrates, crown ethers and/or cryptands.

Particularly preferred complexing agents for silver are EDTA, DTPA and N,N,N',N'-tetrakis-(2-hydroxypropyl)ethylene diamine. The complexing agent should form a soluble complex with plating metal ions in aqueous solution under the pH conditions of the plating solution.

A suitable complexing agent for bismuth is chloride, and it is generally unnecessary to use a multidentate (ie bi- or higher-dentate) ligand complexing agent for bismuth.

The complexing agent is preferably used either in stoichiometric equivalent amounts or in a stoichiometric excess so that all the plating metal ions may be complexed. By stoichiometric we mean equimolar. Preferably the complexing agent is present in a higher molar concentration than the silver ions, the molar ratio preferably being (at least 1.2):1, more preferably (at least 2.0):1, more preferably (at least 3):1.

Suitable tarnish inhibitors for use in all aspects of the present invention include for example:

(a) fatty acid amines, preferably having at least 6 carbon atoms, most preferably at least 10 carbon atoms and generally no greater than 30 carbon atoms, they may be primary, secondary, tertiary, diamines, amine salts, amides, ethoxylated amines, ethoxylated diamines, quaternary ammonium salts, quaternary diammonium salts, ethoxylated quaternary ammonium salts, ethoxylated amides and amine oxides. Examples of the primary, secondary and tertiary amine-type corrosion inhibitors are ARMEEN™ (™ denotes trademark). Examples of the subsequent amine-type

corrosion inhibitors are respectively DUOMEEN™, ARMAC™/DUOMAC, ARMID™, ETHOMEEN™, ETHODUOMEEN™, ARQUAD™, DUOQUAD™, ETHOQUAD™, ETHOMID™, ARONOX™, all supplied by Akzo Chemie.

(b) Purines and substituted purines.

(c) N-acyl derivatives of sarcosine, such as the SARKOSYL range of products supplied by Ciba-Geigy.

(d) Organic polycarboxylic acids such as Reocor 190 supplied by Ciba-Geigy.

(e) substituted imidazoline in which substituents are for example hydroxyl C_{1-4} alkyl amino or carbonyl-containing groups. Examples include AMINE O, produced by Ciba-Geigy, especially in combination with a N-acyl sarcosine of category (c)

(f) alkyl or alkyl benzyl imidazoles, eg undecyl imidazole in which the alkyl group has up to 22 carbon atoms, preferably no greater than 11 carbon atoms and in which the alkyl or benzyl groups are optionally substituted.

(g) benzimidazoles, especially alkylaryl benzimidazoles in which the alkyl group has up to 22 carbon atoms, preferably no greater than 10 carbon atoms and in which the alkyl or benzyl groups are optionally substituted, for example 2-(p-chlorobenzyl) benzimidazole which is particularly preferred.

(h) Phosphate esters such as EMCOL PS-413, supplied by Witco.

(i) Optionally substituted triazole derivatives such as REOMET 42, supplied by Ciba-Geigy. Examples are benzo triazole, tolyl triazole and alkyl substituted triazole derivatives having a carbon number on the alkyl group of from 1 to 22, preferably from 1 to 10.

(j) substituted tetrazoles, such as 5(3(trifluoromethyl phenyl)) tetrazole, is also a preferred example.

The choice of tarnish inhibitor will depend to some extent upon the metal of the plated metal surfaces, but

this will be clear to a person skilled in the art. For example, if the tarnish inhibitor is to be incorporated into a gold plating bath, the tarnish inhibitor may be a chloride salt, however, in contrast, using a silver plating bath, chloride salts may not be used as they will result in formation of an insoluble silver chloride precipitate.

The tarnish inhibitor is preferably water soluble so that the solution is an aqueous solution. However, water immiscible tarnish inhibitors may be used although it may be necessary to include a surfactant/cosolvent in the solution.

This invention has been found to provide considerable advantages in preventing tarnishing and conferring humidity resistance on the bare boards produced so that additional protection is provided between the bare board manufacture stage and the component-attachment stage. Solderability is found to be enhanced.

A suitable pH for a silver plating composition may be from 2 to 12, but is preferably from 4 to 10. Thus, the composition may be acidic, up to pH 7. Alternatively, the composition may be alkaline, and have a pH of greater than 7, or even greater than 7.5. A bismuth plating solution usually has a low pH of 1 or less.

A buffering agent may be included in the plating composition to ensure that the pH of the composition is within the desired range. As the buffering agent, any compatible acid or base may be included. A compatible acid or base is an acid or base which in the amounts required in the composition does not result in the precipitation out of solution of the silver ions and/or complexing agent. For example hydrogen chloride is unsuitable for a silver plating composition as it forms an insoluble silver chloride precipitate. Suitable examples include sodium or potassium hydroxide or a carbonate salt, or where acids are required, suitable acids may include citric acid, nitric acid or acetic acid. Borates phthalates, acetates, phosphonates may be used but the buffer should not result

in precipitation of the metal salts and preferably does not inhibit the plating rate. An appropriate buffer will be dependent on the desired working pH.

The plating composition may include optional ingredients such as surfactants or wetting agents to improve the coating uniformity. Where surfactants are included, preferably they are introduced into the composition in an amount such that in the plating bath, they will be present at a concentration of from 0.02 to 100 g/l. Preferably they will be incorporated at a concentration of from 0.1 to 25 g/l and most preferably at a concentration of from 1 to 15 g/l. Any standard surfactant or wetting agent useful in a plating bath may be used. Nonionic surfactants are preferred. Particularly preferred surfactants are alkyl phenol ethoxylates, alcohol ethoxylates and phenol ethoxylates such as *Synperonic NP9 (ex ICI), *Synperonic A14 (ex ICI) and *Ethylan HB4 (ex Harcros), respectively (*denotes trade name).

A further optional ingredient which can be included in the plating baths of the present invention are grain refiners. Grain refiners improve the appearance of the plated metal surfaces by causing formation of smaller crystals of plated metal having a more densely packed structure. Suitable examples of grain refiners include lower alcohols such as those having from 1 to 6 carbon atoms, for example isopropanol and polyethylene glycols, for example PEG 1450 (Carbowax® Union Carbide). Grain refiners may be incorporated in the composition in amounts from 0.02 to 200 g/l. More preferably, if a grain refiner is included, it will be at concentrations of from 0.05 to 100 g/l and most preferably from 0.1 to 10 g/l. Any non-aqueous solvent should be present in amounts below 50% by weight of the composition, preferably below 30% by weight or even below 10% or 5% by weight of the plating composition.

Other non-active, non-interfering components may be included such as defoamers especially for spray applications (eg, A100 supplied by Dow), dyes etc.

The balance in the composition is water. Deionised water or other purified water which has had interfering ions removed, is used in the plating composition used in the process of the invention.

In order to form the plating composition for use in the processes of the present invention, preferably a solution is firstly prepared comprising deionised water, complexing agent as defined above, and any buffering agent, optionally with the other optional ingredients, and a salt of the more electropositive metal is added as an aqueous solution to the other components which have been formed into a pre-mix. It has been found that this is the most advantageous way to prepare the solution because trying to dissolve the metal salt directly into the plating composition is relatively time consuming and, where the metal is silver, tends to be more vulnerable to photo-reaction which results in precipitation of silver ions out of solution, as a dark precipitate.

Preferably the pH of the composition to which a silver salt is added will be from pH 3 to 10, most preferably from 4 to 8.

The components are mixed until they have substantially dissolved. The use of heat for silver dissolution is disadvantageous because again, it may tend to cause the formation of a dark silver precipitate.

After contact of the bare board with the solution comprising tarnish inhibitor, the board is dried. Preferably, there will be no post-rinse step between contact of the board with the solution and drying.

Drying may be by any means, but is generally using warm air, for example treated metal may be passed through a drying oven.

The coating obtained using the method of the present invention produces a surface which is considerably more

uniform and even than that obtained in the conventional HAL processes and, compared with organic protection, the coating is more resistant to soldering operations. Furthermore, the process of this invention is less expensive and simpler than use of the nickel/gold process.

In the subsequent component-attachment stage, the components are soldered onto the plated pads and/or through-holes of the bareboard. The metal of the pad(s) and/or through-holes (generally copper) and plating metal, usually silver, and/or the plating metal and solder may tend to intermix. The bond formed with the components has good electrical conductivity and good bond strength.

After component attachment, finished boards having components attached over the plated layer of the present invention, do not suffer joint reliability problems as do those boards formed using a nickel/gold step.

Example 1

A composition was prepared in which 50g EDTA and 20.4g of solid sodium hydroxide were mixed with sufficient water to dissolve them. A solution comprising 1g silver nitrate in deionised water was subsequently added to the premixture comprising EDTA and sodium hydroxide solution and deionised water was added to 1 litre. Copper double sided circuit boards, having a variety of surface mount feature and plated through holes of various diameter were coated with the silver solution using the following procedure.

Boards were chemically brightened in an aqueous solution of 20% v/v H_2O_2 (35%), 0.5% v/v H_2SO_4 (96%), 2.5% 1,4-butanediol for 1 minute. A tap water rinse was then employed, followed by an acid rinse in 10% H_2SO_4 for 1 minute. The boards were given a further water rinse, then immersed in the silver plating solution at 40°C for 4 minutes. After removal from the bath, the boards were rinsed with water and warm air dried. Copper areas of the board were coated with a bright, even silver deposit.

Coated boards were subjected to three passes through a typical IR silver paste reflow profile - see figure 1,

then wave soldered using NR300, an Alpha Metals VOC free, no clean flux. 100% filing of the plated-through holes with solder was achieved.

Furthar boards were stored in a humidity cabinet at 40°C/93% RH for 24 hours before being passed through 3 IR reflow profiles. These boards showed a slight degree of tarnishing on the silver coating. However 100% hole filling was still achieved during subsequent wave soldering with NR 300 flux.

Example 2

A silver plating solution was prepared by forming a solution comprising 50g EDTA, 20.4g NaOH, 14g Ethylan HB4 (Akros Chemicals), 3g Crodamet 02 (Croda Chemicals) in 800mls deionised water. To this solution was added a solution of 1g $AgNO_3$ in 100 mls deionised vater. The pH was adjusted to 6.8 by addition of dilute $NaOH/HNO_3$, then made up to 1 litre with deionised water.

Double sided bare copper boards were coated with the above solution using the procedure as described in example 1. 100% filling of plated through holes with solder was achieved during wave soldering with NR300 flux after passage through 3 IR reflow profiles.

Boards stored at 40°C/93%RH for 24 hours prior to passage through 3 IR reflow profiles showed no evidence of tarnishing and soldered well during wave soldering trials, giving 100% hole filling.

Example 3

Double sided bare copper boards were coated using the bath composition and procedure as described in example 1. Following removal of the boards from the silver plating solution and rinsing, the boards were immersed in a solution of 4g Reomet 42 (Ciba-Geigy) in 1 litre deionised water (pH 7) for 1 minute at room temperature. The boards were then rinsed in tap water and warm air dried. A bright even silver coating was produced.

The coated boards were stored at 40°C/93% RH for 24 hours then passed through 3 IR paste reflow profiles. The

boards showed no evidence of tarnishing, and soldered well when wave soldered using NR 300 flux.

Example 4

Coupons of copper strip (5cm x 1cm) were coated with the silver coating as described in example 2. In addition, further samples were coated with immersion tin, 63/37 Sn/Pb and two competitors solderability preservative coatings based on substituted benzimidazole chemistry. The following coating procedures were applied for the various samples:-

Immersion Tin Coating

Coupons were etched in an aqueous solution of $Na_2S_2O_8$ (5%), H_2SO_4 (5%) for 2 minutes, rinsed with tap water, then rinsed with 10% H_2SO_4 for 1 minute and then rinsed with deionised water. The coupons were then immersed in an immersion tin plating solution comprising 33g/ℓ Sn $(BF_4)_2$ 150 g/ℓ thiourea, 20 g/ℓ fluoroboric acid and 5 g/ℓ Synperonic NP9 (ex ICI) in deionised water, for 1 minute at room temperature. The coupons were then rinsed with deionised water and warm air dried.

Sn/Pb Coating

Coupons were etched in an aqueous solution comprising $Na_2S_2O_8$ (5%) and H_2SO_4 (5%), rinsed with tap water then with 10% H_2SO_4 and then with deionised water. The coupons were warm air dried. Alpha NR300 flux was then applied to each coupon. The coupons were then coated 63/37 Sn/Pb by immersion in molten solder at 250°C for 3 seconds.

Azole 1 and Azole 2

Coupons were etched and rinsed as for the immersion tin samples. Coupons were then immersed in the solution containing the azole at 40°C for 90 seconds. After removal from the azole containing solution, the coupons were rinsed with deionised water, and warm air dried.

The coupons were subjected to a variety of different pre-treatments.

A. No pre-treatment.

B. Passage through 3 solder paste reflow profiles.

C. Storage at 40°C/93% RH for 96 hours.

D. Storage at 40°C/94% RH for 96 hours, then 3 solder paste reflow profiles.

E. Storage at 150°C for 2 hours.

Samples were then soldered using a meniscograph with NR300 flux.

The meniscograph test method monitors the solderability by measuring the net force acting between specimen and solder. The coatings are assessed by the length of time to reach zero wetting force, and the size of the equilibrium wetting force. To achieve good results in wave soldering a short wetting time and high equilibrium wetting force are preferred.

The table below shows the wetting times in seconds and wetting forces after 2 seconds immersion in mN/mm for various copper coated samples.

TABLE 1

Coating	Pre-Treatment	Wet time/sec	Wetting force at 2 seconds
Example 2	A	0.7	0.429
Example 2	B	0.8	0.444
Example 2	C	0.7	0.429
Example 2	D	0.7	0.441
Example 2	E	0.8	0.438
Tin	A	0.9	0.488
Tin	B	> 5	-0.028
Tin	C	> 5	0.008
Tin	D	> 5	-0.148
Azole 1	A	0.8	0.439
Azole 1	B	0.9	0.412
Azole 1	C	0.9	0.443
Azole 1	D	0.9	0.426
Azole 1	E	1.0	0.421
Azole 2	A	0.9	0.449
Azole 2	B	1.0	0.417
Azole 2	C	0.9	0.466
Azole 2	D	1.1	0.310
Azole 2	E	1.2	0.296
Sn/Pb	A	0.8	0.475
Sn/Pb	B	0.8	0.501
Sn/Pb	C	0.8	0.492
Sn/Pb	D	0.8	0.474
Sn/Pb	E	0.8	0.492

As can be seen from above, the silver coatings prepared according to this invention have shorter wetting times and higher wetting forces than the Sn and benzimidazole alternative and retain these properties more readily after humidity and heat treatment.

Example 5

A displacement bismuth plating composition was prepared comprising 3.9g bismuth oxide, 183.1g hydrogen chloride (as 37% solution), 490.5g glycolic acid (70%

solution), 265.4g (50% sodium hydroxide solution), 0.077g potassium iodide, 0.003g Synperonic NP9 (ex ICI) and 4g 2p-chlorobenzyl benzimidazole, were added to deionised water to make 1 litre of product solution. Bare boards having copper pads and copper through holes were chemically brightened as described in example 1, then immersed in the plating baths for 2 minutes at 70°C. A coating of bismuth was formed on the surface of the copper having a thickness of 0.05μm. Subsequent solderability and tarnish resistance tests carried out on the plated bare boards showed good results for solderability and tarnish resistance.

Example 6

Double sided bare copper boards were bright etched in an aqueous solution of 50% v/v HNO_3, 10% H_2SO_4 10% H_3PO_4, 1% HCl for 1 minute at room temperature. Boards were then rinsed in tap water followed by 10% H_2SO_4 for 1 minute. After a further water rinse, boards were immersed in silver plating bath described in example 2 for 4 minutes. at 45°C. Boards were then water rinsed and warm air dried.

The coated boards were stored at 40°C/93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing and soldered well when wave soldered using NR 300 flux.

Example 7

A silver plating bath was prepared by forming a solution comprising 64.8g diethylene triamine penta-acetic acid, 23.0g NaOH, 14g surfactant Ethylan HB4 (Akros Chemicals), 2.5g Crodamet 02 an ethoxylated 3° amine compound (Croda Chemicals) in 800mls deionised water. To this solution was added a solution of 1g silver nitrate in 100mls deionised water. The pH of this solution was adjusted to 6.9 by addition of dilute NaOH solution or nitric acid. The volume was then made up to 1 litre using deionised water.

Double sided bare copper boards were coated using the above solution using the procedure as described in Example 1. 100% filling of the plated through holes was achieved

during wave-soldering of the coated boards using Alpha Metals NR300 flux after passage through 3 I.R. reflow profiles showed no evidence of tarnishing, and soldered well during wave-soldering trials giving 100% hole-fill.

Example 8

An immersion silver plating solution was prepared comprising 98.1g deionised water, 1g of nitric acid, 0.1g of silver nitrate, 0.3g of Chemeen C2 (antitarnish) and 0.4g Nazawet DF (solubiliser). The pH was adjusted to 6 using a 50% solution of ethylene diamine. The bath produced an adherent silver deposit on copper coupons which showed good solderability and humidity resistance.

Example 9

A bismuth plating solution was prepared containing bismuth trioxide 2.1% wt., hydrochloric acid (22°Be) 46.73% wt., glycollic acid (70%) 49.5% wt., potassium chloride 0.07 % wt., polyethylene glycol 600 0.1% wt., Chemax Chemeen C2 0.2% wt., distilled water 1.2% wt. and tartaric acid 0.1% wt. A further solution was prepared from which the Chemeen C2 was omitted. Samples of copper clad printed circuit material were plated in each of the solutions. These plated samples were then placed in a humidity chamber for 16 hours at 60°C and 95% relative humidity.

After this exposure the samples were examined, and those prepared in the solution without the Chemeen C2 were heavily tarnished. The samples prepared in the solution containing the tarnish inhibitor had a good appearance with minimal oxidation, and when tested showed good solderability.

4. Brief Description of Drawings

figure 1 (which illustrates a suitable example of temperature against time for a reflow pass)

Fig 1

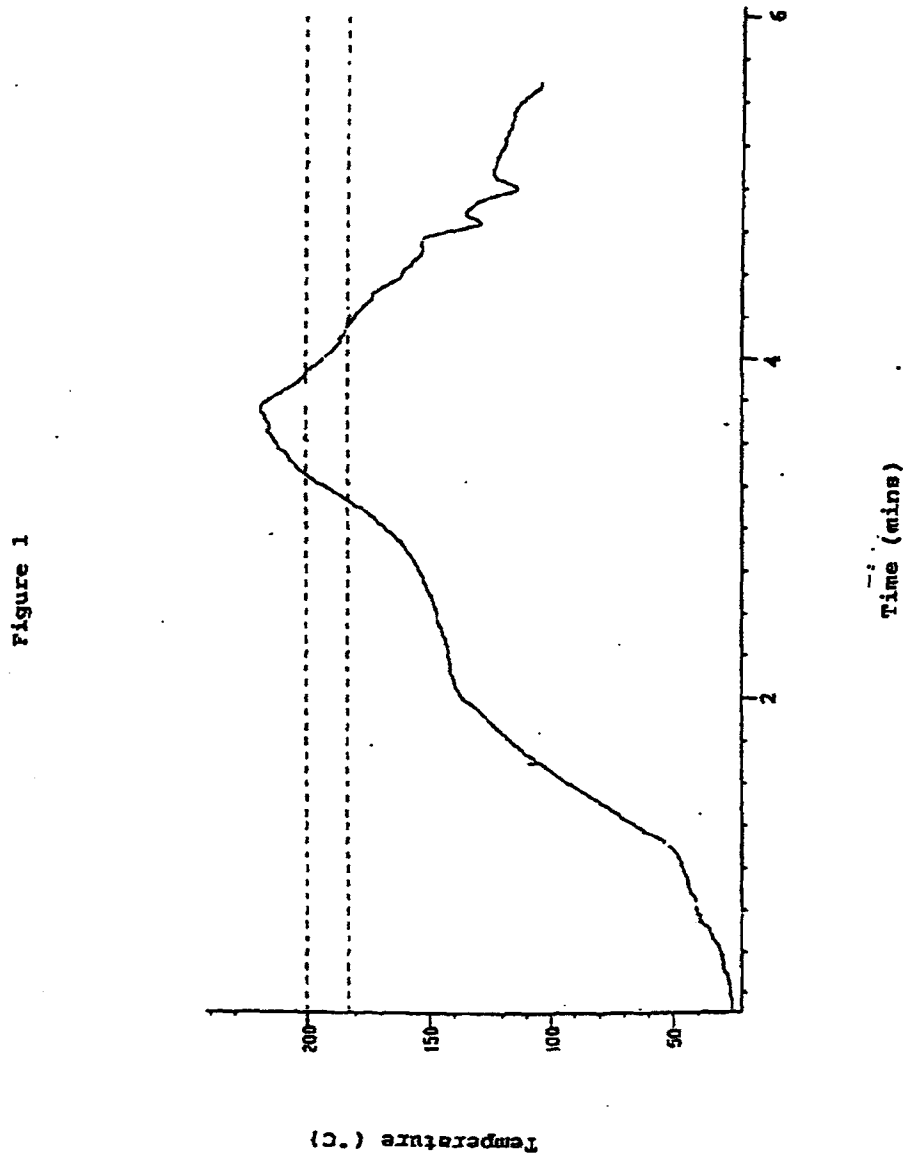

Figure 1

1. Abstract

A process used during manufacture of PCB's comprises protecting metal pads and/or through-holes to provide a tarnish-resistant and solderable coating. In the method the pads and/or through-holes are bright-etched, metal plated, preferably by an immersion process, and treated with a tarnish inhibitor. The tarnish inhibitor may be incorporated into the immersion plating bath. The metal plating is usually with silver or bismuth and the pads and/or through-holes comprise copper.

2. Representative Drawings

Fig 1